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INDUSTRIAL WASTE SURVEY REPORT AT KOBUTA PLANT CHEMICAL DIVISION KOPPERS COMPANY, INCORPORATED, MAY 14 TO JUNE 21, 1952. PART I AND PART II

D. M. Taylor, et al

Environmental Health Center
Cincinnati, Ohio

June 1952

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INDUSTRIAL WASTE SURVEY REPORT
AT
KOBUTA PLANT
CHEMICAL DIVISION
KOPPERS COMPANY, INC.

PB 229 295

MAY 14 TO JUNE 21, 1952

PART I

A STUDY OF THE CHARACTERISTICS OF LIQUID WASTES FROM A CHEMICAL PLANT PRODUCING INGREDIENTS FOR SYNTHETIC RUBBER PRODUCTION AND CERTAIN OTHER ORGANIC CHEMICALS

By

D. M. TAYLOR, Public Health Engineer

R. L. HARRIS, Jr., Asst. Sanitary Engineer

PART II

A STUDY OF THE CHEMICAL AND ODOROUS CHARACTERISTICS OF LIQUID WASTES FROM THE KOBUTA, PENNSYLVANIA PLANT OF THE KOPPERS COMPANY, INC., AND CHEMICAL AND ODOR STUDIES OF WATER SUPPLIES AT MIDLAND, PENNSYLVANIA, WEIRTON, WEST VIRGINIA AND WHEELING, WEST VIRGINIA.

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PART I

INDUSTRIAL WASTE SURVEY REPORT

AT

KOBUTA PLANT
CHEMICAL DIVISION
KOPPERS COMPANY, INC.

MAY 14 TO JUNE 21, 1952

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U.S. DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
ENVIRONMENTAL HEALTH CENTER
CINCINNATI, OHIO

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ABSTRACT

This study was made in connection with the program of industrial waste studies being conducted by the Public Health Service in co-operation with State health departments, other government agencies, and industries. Two major sources of wastes were surveyed, namely: the butadiene plant and the styrene plant. The waste discharge outfalls and waste treatment facilities were also examined. Summaries of each of these studies are given below.

Butadiene Wastes

The butadiene plant contains four complete production units, capable of producing approximately 80 tons/day/unit. Ethyl alcohol (190 proof) is the only major raw material necessary for production, with approximately 2.3 lb butadiene being produced per gallon of alcohol. The process is practically continuous, with most of the operations being automatically controlled.

The major source of process wastes is the high-pressure ethanol still tails. Minor wastes are the chlorex recovery still tails and drainage from the tank pads, compressors, converter pads, tank car washings, and loading area. The ethanol still tails are treated, while all the other wastes are discharged, along with cooling and storm water, to the Ohio River. These ethanol still tails consist mostly of process water, containing organic compounds produced in the process, which have boiling points higher than water, and other organic compounds which have not been completely removed in the recovery systems. All of the other wastes are

considered too dilute for treatment and are discharged with cooling water directly to the main plant outfall.

Equal portions of samples were collected at hourly intervals over 8 and 24 hour periods and composited.

The daily average volumes, daily average net quantities of waste constituents, and unit volumes and quantities of waste constituents prior to treatment are summarized as follows:

	Wastes		
	Concentrated	Dilute	Total
Flow, MGD	0.98	63.69	64.67
Net waste constituents:			
Weighted threshold odor (cold)(1)	22,500	43,500	66,000
Oxygen consumed, lbs/day ($K_2Cr_2O_7$)	73,600	5,700	79,300
B.O.D., 5-day, lbs/day	38,300	3,850	42,150
Unit volumes, gal/ton butadiene	4,080	265,000	269,080
Unit quantities, per ton butadiene:			
Weighted threshold odor (cold)(1)	94	181	275
Oxygen consumed, lbs.	307	24	331
B.O.D., 5-day, lbs.	160	16	176

(1) Product of odor value and flow in MGD.

Styrene Production and Wastes

Styrene is produced at the Koppers Company plant at Kobuta by a modified Dow process. The process consists of the production of ethylene by the dehydration of diethyl ether and by the cracking of crude petroleum, the purification of ethylene, the processing of motor fuel and light oil to obtain benzene, the alkylation of benzene with ethylene to produce ethyl-benzene, and dehydrogenation of ethyl-benzene to produce styrene, and the purification of product styrene. Average production is about 140 tons of styrene per day.

During the course of the survey, samples were collected at eight locations in the styrene process waste system, tributary to the plant's waste treatment facilities, at eight locations within the styrene production area in the uncontaminated waste system tributary to the main outfall, and at one location where a dilute waste was discharged from the styrene production area directly to Raccoon Creek. Results obtained from examination of these wastes are summarized below.

Total Net Quantities of Waste Constituents
Discharged Daily from Styrene Production Operations

	Flow MGD	Weighted Threshold Odor (Cold)(1)	Oxygen Consumed lb/day	B.O.D. lb/day
Concentrated wastes tributary to aerator for treatment	1.46	9,110	6,440	3,740
Oil cracking concentrated wastes tributary to butadiene waste oil skimmer for treatment	0.22	10,600	28,600	16,700
Total concentrated wastes, subsequently treated	1.68	19,710	35,000	20,400
Dilute wastes tributary to main outfall (untreated)	43.3	2,530	7,000	2,800
Dilute wastes discharged directly to Raccoon Creek (untreated)	8.4	150	0	260
Total dilute wastes, discharged untreated	51.7	2,680	7,000	3,060
Grand Total(2)	53.4	22,390	42,000	23,500

(1) Product of odor value and flow in MGD.

(2) Total concentrated wastes, subsequently treated, plus total dilute wastes, discharged untreated.

The oil cracking concentrated wastes which are tributary to the butadiene waste oil skimmer for treatment have a volume of only 0.22 MGD, but contribute some 40 per cent of the weighted threshold odor and some 70 per cent of both the oxygen consumed value and the B.O.D. value of all wastes resulting from the styrene production operations.

Based on a daily production rate of 140 tons of styrene, the following tabulation shows unit values of the various waste constituents per ton of styrene produced.

Raw Waste Unit Values per Ton of Styrene

	Volume gallons	Weighted Threshold Odor Units	Oxygen Consumed pounds	B.O.D. pounds
Concentrated wastes tributary to aerator for treatment	10,420	65	46	27
Oil cracking wastes tributary to the butadiene waste oil skimmer for treatment	1,540	76	204	119
Total concentrated wastes, subsequently treated	12,000	141	250	146
Dilute wastes tributary to main outfall (untreated)	309,000	18	50	20
Dilute wastes discharged directly to Raccoon Creek (untreated)	59,000	1.1	0	2
Total dilute wastes discharged untreated	368,000	19	50	22
Grand Total (2)	380,000	160	300	168

(2) Total concentrated wastes, subsequently treated, plus total dilute wastes, discharged untreated.

WASTE LINES AND TREATMENT

There are six outfall waste lines discharging into the Ohio River. Four of them actually discharge to Raccoon Creek which flows into the Ohio River. The concentrated (contaminated) wastes are treated and finally flow from a lagoon to Raccoon Creek, while the dilute (uncontaminated) wastes flow directly into Raccoon Creek or the Ohio River.

(1) 8" Line to Raccoon Creek - This line carries the sanitary wastes from the plant and Kobuta Village. Primary treatment, with an Imhoff tank and sludge drying beds, is provided.

(2) 18" Line to Raccoon Creek - These wastes consist of quench water for emergency blowdowns from the ethylbenzene and oil cracking plants.

(3) 30" Line to Raccoon Creek - These wastes include those from the polystyrene plant and cooling water from the oil cracking plant.

(4) Main Outfall - This line carries all the dilute wastes from butadiene and styrene operations, other than those to the 30" and 18" lines to Raccoon Creek. It also includes wastes from such miscellaneous areas as the water treatment plant, power house and maintenance areas.

(5) Phthalic Anhydride Waste Line - These wastes consist, for the most part, of cooling water and are discharged into the Ohio River. The concentrated wastes lagoons were not functioning properly during the period of the survey and some strong wastes were seeping through the walls to the Ohio River.

(6) Lagoon Outfall - The combined treated wastes from butadiene and styrene operations are discharged to a lagoon, whose effluent flows into Raccoon Creek.

There are two separate waste treatment systems.

The high pressure ethanol still tails from the butadiene plant and the oily wastes from the oil cracking unit of the styrene plant are combined and passed through an oil skimmer. The oil layer is drawn off for fuel, while the water layer is passed through a neutralizing tank where the pH is raised from 4.4-4.6 to 5.7-11.4, with slaked lime. The neutralized effluent then passes through two stills, operating in parallel, with 3 to 5 per cent of the total wastes being condensed as overhead. The condensate passes through a decanter, with the oil going to fuel and the water layer back to the oil skimmer inlet or process re-use. The still tails are discharged to a lagoon.

Concentrated wastes are pumped from various sumps in the styrene plant to a common wet well from which they are pumped to an aerator. They are sprayed over slats with air being blown up through them by fans. Recirculation, with pumps and separate spray nozzles, is available. The effluent then flows to the lagoon along with the treated butadiene wastes.

The estimated capacity of the lagoon is 14 MG. The theoretical holding time is 4.8 days, based on an average waste flow of 2.92 MGD.

Equal sample portions were collected at hourly intervals for compositing. Both 24 and 8 hour composite samples were taken. Samples of raw river water, used in the plant, were taken for the purpose of calculating net waste values.

Quantitative odor values are expressed as weighted odor values, all of which are products of odor values and flows in MGD.

The over-all waste removing efficiencies of the treatment units for the butadiene and oil cracking processes were as follows:

Waste Removal Efficiencies - Per Cent

	Weighted Threshold Odor		Oxygen Consumed ($K_2Cr_2O_7$)	B.O.D. 5-day
	Cold	Hot		
Oil skimmer	29	62	24	13
Neutralizer	-17(1)	5	-10(1)	15
Stills	73	24	31	22
Total	85	91	45	58

(1) Indicates increase rather than decrease. Probably due to inherent sampling difficulties.

The average waste removal efficiencies of the aerator were as follows:

Waste Removal Efficiencies of Aerator - Per Cent

	With Recirculation	Without Recirculation
Weighted threshold odor:		
Cold	84	95
Hot	95	91
Oxygen consumed ($K_2Cr_2O_7$)	65	75
B.O.D., 5-day	70	90

The recirculation ratio was 1.55 : 1

The average waste removal efficiencies of the lagoon were as follows:

Removal of Waste Constituents in Lagoon - Per Cent

Weighted threshold odor:	
Cold	67
Hot	75
Oxygen Consumed ($K_2Cr_2O_7$)	32
B.O.D., 5-day	19
Oils	80

The percentage removals of waste constituents by all treatment methods from the concentrated (contaminated) and total wastes, from the butadiene and styrene plants, were as follows:

Per Cent Removal of Waste Constituents

	Concentrated Wastes	Total Wastes
Weighted threshold odor:		
Cold	98	78
Hot	99	88
Oxygen consumed ($K_2Cr_2O_7$)	58	45
B.O.D., 5-day	48	43

The total gross and net quantities of waste constituents discharged from the plant (butadiene, styrene, polystyrene and phthalic anhydride process operations), during the period of the survey, were as follows:

Quantities of Waste Constituents

	Gross	Net
Weighted threshold odor:		
Cold	23,500	21,900
Hot	14,100	12,400
Oxygen consumed ($K_2Cr_2O_7$) lbs/day	82,700	56,200
B.O.D., 5-day, lbs/day	34,200	32,000
Phenols, lbs/day	410(1)	310(1)
Oils, lbs/day	8,270	2,320

(1) See discussion of phenol results on page 124 regarding lagoon effluent wastes. Also total wastes on page 125.

The volumes of industrial liquid wastes flowing from the plant are summarized as follows:

Volumes of Liquid Wastes Discharged from Plant

	MGD
Concentrated Wastes to Treatment (Contaminated):	
Oil cracking	0.22
Butadiene	1.19
Total to stills	1.41
Total from stills	1.46
Styrene from aerator	1.46
Total from lagoon	2.92
Dilute wastes (Uncontaminated);	
Main outfall	127.
30" line to Raccoon Creek	8.4
18" line to Raccoon Creek-	Relatively insignificant
8" " " " "	Not considered
Phthalic anhydride	3.
Total dilute	138.4
Total industrial liquid wastes	141.32

GENERAL INFORMATION

1. Organization of Survey

This survey was a co-operative endeavor of the Environmental Health Center and Ohio-Tennessee Drainage Basin Office of the Public Health Service, the Pennsylvania Department of Health, the West Virginia State Water Commission, the Koppers Company, and the Synthetic Rubber Division of the Reconstruction Finance Corporation. The Industrial Wastes Section of the Environmental Health Center served as a representative of the Pennsylvania Department of Health in obtaining wastes data within the Koppers Kobuta plant. The Pennsylvania Department of Health made a special stream study on the Ohio River, at the same time, above and below the plant, for the purpose of observing the effect of the industry's wastes on the stream.

During the latter part of the survey period, the State Water Commission of West Virginia collected samples from the Ohio River at points downstream from the Pennsylvania state border.

The Ohio-Tennessee Drainage Basin Office of the Water Pollution Control Division and the Physics and Chemistry Section of the Environmental Health Center participated by furnishing personnel to make carbon filter studies in relation to odor problems in the river water. The Synthetic Rubber Division representatives furnished advice and counsel at the joint meetings, with regard to survey objectives and data.

Public Health Service engineers supervised the waste survey within the plant. Analytical determinations were performed in mobile laboratories by Public Health Service chemists. Koppers Company furnished utility connections for the mobile laboratories, aided personnel in becoming familiar with plant operations, supplied pertinent operational data, and furnished sampling equipment and personnel. An engineer from the Ohio-Tennessee Drainage Basin Office collected the carbon filter samples in the field, while chemists of the Physics and Chemistry Section made the analyses of these samples in the Cincinnati laboratories of the Public Health Service.

2. Dates of Survey

May 14 to June 21, 1952.

3. Purpose of Survey

The objectives of this survey were as follows: to determine the characteristics and quantities of total liquid wastes discharged from the butadiene and styrene areas of the plant; study the waste treatment facilities with particular reference to their efficiencies; study the sources and characteristics of the concentrated wastes; and examine the so-called uncontaminated waste system for the purpose of determining whether or not it would be practical to divert certain wastes to the waste treatment units.

4. Personnel Participating

Koppers Company, Inc.

Kobuta Plant

T. H. Insinger, Chief Chemist
C. F. Bell, Supt., Utilities
J. J. McGovern, Asst. Chief Chemist
C. K. Nagy, Laboratory Supervisor
J. N. Strickler, Jr., Chemical Engineer
L. F. Hellerman, Group Leader

Research Department

W. W. Hodge

Reconstruction Finance Corporation

Synthetic Rubber Division

R. E. Rostenbach, Technologist

Pennsylvania Department of Health

J. R. Harvey, District Engineer, Meadville District

Public Health Service

Industrial Wastes Section, Environmental Health Center

H. H. Black, Chief
D. M. Taylor, Public Health Engineer
R. L. Harris, Asst. Sanitary Engineer
S. Soneda, Asst. Sanitary Engineer
W. W. Walker, Sanitary Chemist
C. R. Hirth, Physical Science Aide
M. D. Currey, Automotive Mechanic

Physics and Chemistry Section, Environmental Health Center

F. M. Middleton, Scientist
H. Braus, Chemist

Ohio-Tennessee Drainage Basin

W. W. Towne, Basin Engineer
H. W. Wolf, Asst. Sanitary Engineer
C. H. Hull, Sr. Asst. Sanitary Engineer

5. Location of Plant

This chemical plant is located on the south bank of the Ohio River in Beaver County, Pennsylvania, about thirty miles downstream from Pittsburgh and about six miles below the mouth of the Beaver River.

6. Employees

The number of employees was approximately 1350, which included office and technical staff.

7. Raw Materials

Ethyl alcohol is the raw material for manufacturing butadiene. Styrene is made from ethylene and benzene. Light oil and/or benzol are purchased for benzene production. Ethylene may be made from ether, propane, ethyl alcohol, or oil (cracking).

8. Products

The principal products are butadiene and styrene.

9. Production

There are four butadiene units, each capable of producing about 29,000 tons per year. The styrene plant was originally designed to produce 38,000 tons a year, but facilities have been expanded to produce about 50,000 tons a year.

All of the butadiene was being shipped to synthetic rubber plants (GR-S). A large part of the styrene was also shipped to synthetic rubber plants, the remainder being made into polystyrene or sold to private consumers.

10. Plant Operations

Three of the four butadiene units were in operation during the period of the survey and it is doubtful whether all four units will ever be in operation simultaneously. Whenever a unit is in production, it operates 24 hours a day, 7 days a week. The styrene plant operates 24 hours a day, 7 days a week, and 52 weeks a year.

11. Water Supply

The two sources of water were the Ohio River and three company wells. The river water was used for cooling purposes, process water and boiler feed water. The well water was chlorinated and used for sanitary and cooling purposes.

The river water pumping station is located on the river bank, upstream from the plant. It is provided with six pumps, each capable of delivering 20,000 gpm. There are coarse screens ahead of the pumps and there is a Brassert strainer in the pressure side of the line after each pump. River water pumpage averaged 140 MGD during the period of the survey.

Approximately 2.8 per cent of the river water is treated for process and boiler plant purposes. It is treated with chemicals, passed through Spaulding precipitators,(3) then anthrofilt filters,(6) and finally softened in open Permutit zeolite beds.(6) Approximately 79 per cent of the raw water going to the treatment plant is used for the boiler plant, 4 per cent for process purposes, and 17 per cent for backwash and rinse.

The average daily volume of well water pumped during the month of May, 1952, was 0.96 MGD. There was a standpipe on the system and the operating schedule called for continuous pumping from one well, plus intermittent supplemental pumping from another. The third well stood in reserve. Koppers Company, Inc., was supplying sanitary water for Kobuta Village, which was a nearby housing project, immediately adjacent to plant property (west side) on the river bank, downstream from the plant. There were approximately 500 people in Kobuta Village. The total daily water consumption for sanitary purposes was estimated to be about 0.19 MGD, or about 19.8 per cent of the total well water pumped. The remaining 0.77 MGD were used for cooling purposes in process units.

12. Process Waste Disposal

All water-carried process wastes from the plant discharge to the Ohio River, or to Raccoon Creek which in turn flows into the Ohio River. The more concentrated wastes are treated before discharge into a lagoon which empties into Raccoon Creek. A 30-inch outfall sewer to Raccoon Creek carries polystyrene wastes and cooling water from the oil cracking plant. An 18-inch outfall line from the blowdown sump carries a small amount of water to Raccoon Creek. All of the remaining water-carried wastes from the butadiene and styrene plants are discharged directly to the Ohio River through the main outfall sewer. These last wastes consist mainly of cooling water plus storm water, boiler house and water treatment plant waste water, maintenance area drainage, and chlorex still tails from the butadiene units.

The phthalic anhydride plant is located on another part of the Koppers Company property. The concentrated wastes from this plant are lagooned with enough volume and area to prevent overflow. The last lagoon sections were new, and porous enough to allow seepage to the river. If these porous walls do not plug up in time, it will be necessary to line them with solid material to prevent seepage to the river. The remainder of the plant wastes, which are relatively uncontaminated, are discharged to the Ohio River about 300 feet above the pumping station.

Process wastes will be discussed in more detail in a later section.

13. Sanitary Sewage

All sanitary sewage from the plant and Kobuta Village flows through an Imhoff tank, and thence to Raccoon Creek. The sludge is dried on sand beds.

14. Report Organization

This report is presented in three sections, as follows:

A. Butadiene operations and wastes.

B. Styrene operations and wastes.

C. Waste lines and treatment.

Sections A and B describe the operational process, and sources, characteristics, total quantities, quantities per unit of production, etc., of water-carried wastes originating from specific plant operations. Section C describes the characteristics, quantities, and methods of disposing of wastes discharged from general areas.

Only a limited number of samples were collected, during the period of the survey, at numerous points in the waste systems. This was necessitated by the desire to locate as many wastes as possible which were concentrated and might be diverted to waste treatment units.

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SECTION A - BUTADIENE OPERATIONS AND WASTES

Ethyl alcohol is converted to butadiene, which in turn is used in making GR-S synthetic rubber elsewhere. The major source of water-carried wastes is the ethanol still tails. Process operations, survey procedures, wastes analyses, etc., are given below.

DESCRIPTION OF PROCESS

Ethyl alcohol (190 proof) is the only major raw material necessary for the production of butadiene by this method. The chemical reaction involved in the process may be summarized as follows:

Reaction in Acetaldehyde Converters:

$$C_2H_5OH \xrightarrow[\text{catalyst}]{} CH_3CHO + H_2$$

This conversion, carried out in a vapor phase over a catalyst, also results in the formation of appreciable quantities of acetic acid, ethyl acetate, butraldehyde and butanol.

Reaction in butadiene converters:

$$C_2H_5OH + CH_3CHO \xrightarrow[\text{catalyst}]{} C_4H_6 + 2\ H_2O$$

This second conversion, also carried out in a vapor phase over a catalyst, results in the formation of a large number of by-products. Among these are ethylene, ethyl ether, methyl ethyl ether, butylene, butanol, butraldehyde, acetic acid, ethyl acetate, and various other hydrocarbon materials.

The catalysts must be periodically reactivated.

The process flow diagram is shown in Figure A-1. This diagram is simplified and does not show such pieces of equipment as heat exchangers, pumps, compressors, tanks, separators, etc. There are four separate butadiene production units at Kobuta, each one employing the same process of operation.

Butadiene is a liquid, insoluble in water, with a density at -6°C of 0.650, freezing point of -108.9°C, boiling point of -4.8°C, and molecular weight of 54.05 g.

1. Ethanol Still System

This distillation system produces ethanol vapors for conversion to acetaldehyde, and butadiene. Fresh ethanol is fed to the system, which is continuously recovering ethanol from the process streams. There are two parallel groups of stills, each group having a low-pressure still and a high-pressure still. These stills operate continuously and are automatically controlled by instruments. Temperatures, pressures, flows, reflux ratios, and liquid levels are co-ordinated to produce the desired product.

Ethanol (190 proof) is received at the plant by tank car, barge, or truck, and stored in large field tanks. It is denatured with 0.5 per cent acetaldehyde, according to Government Formula SDA-29 modified M. It is fed, as needed, to reflux tanks, where it mixes with recycle ethanol from the process. Ethanol vapor for the acetaldehyde and butadiene converters is withdrawn from the tops of the high-pressure stills.

20

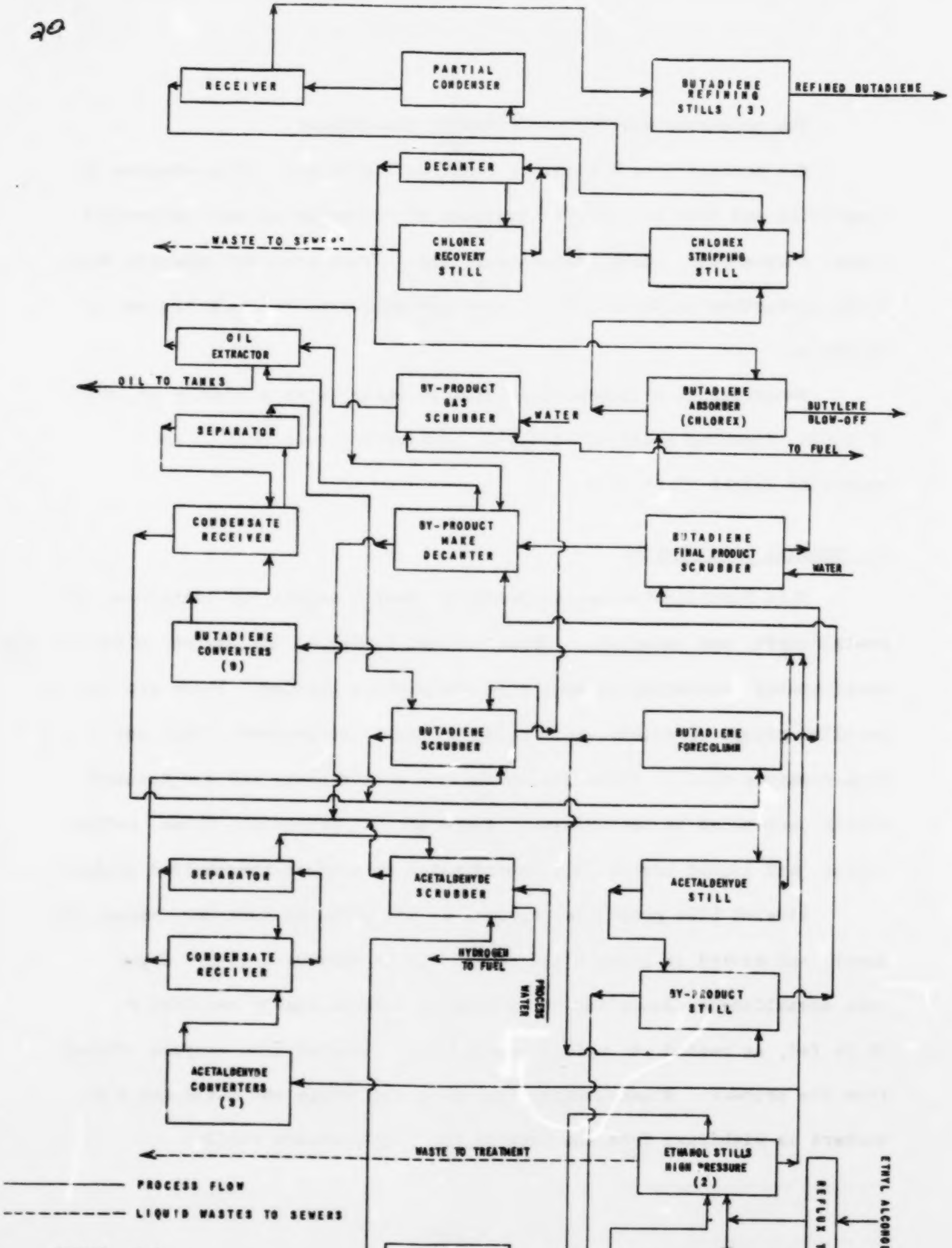
RECEIVER
PARTIAL CONDENSER
BUTADIENE REFINING STILLS (3)
REFINED BUTADIENE
DECANTER
WASTE TO SEWERS
CHLOREX RECOVERY STILL
CHLOREX STRIPPING STILL
OIL EXTRACTOR
OIL TO TANKS
BY-PRODUCT GAS SCRUBBER
WATER
BUTADIENE ABSORBER (CHLOREX)
BUTYLENE BLOW-OFF
SEPARATOR
TO FUEL
CONDENSATE RECEIVER
BY-PRODUCT MAKE DECANTER
BUTADIENE FINAL PRODUCT SCRUBBER
WATER
BUTADIENE CONVERTERS (9)
BUTADIENE SCRUBBER
BUTADIENE FORECOLUMN
SEPARATOR
ACETALDEHYDE SCRUBBER
ACETALDEHYDE STILL
CONDENSATE RECEIVER
HYDROGEN TO FUEL
PROCESS WATER
BY-PRODUCT STILL
ACETALDEHYDE CONVERTERS (3)
WASTE TO TREATMENT
ETHANOL STILLS HIGH PRESSURE (2)
REFLUX TANK
ETHYL ALCOHOL FEED
PROCESS FLOW
LIQUID WASTES TO SEWERS
DECANTER
ETHANOL STILLS LOW PRESSURE (2)

FIGURE A 1

BUTADIENE FLOW DIAGRAM
AT
KOPPERS CO., INC., KOBUTA, PA.

ENVIRONMENTAL HEALTH CENTER

Feed, consisting of ethanol and water, from the base of the by-products removal still (described more fully in a later section) enters the base of the low-pressure stills where it is heated by outside vertical calandrias, condensing vapors from the high-pressure stills, and sparger steam.

The entire overhead vapor from the low-pressure stills, consisting of ethanol and water, is sent to condensers and flows to reflux and feed tanks. Only a portion of the ethanol is removed by the low-pressure column, so the residues from the low-pressure columns are pumped through heat exchangers to the high-pressure columns.

The high-pressure columns are entirely heated by direct steam. Vapors (ethanol and water) not required for acetaldehyde and butadiene conversion are condensed in heat exchangers and then flow to reflux.

The residues from the base of the high-pressure stills contain all the excess water formed in the process and added to the process at various points. There is also a small amount of acetic acid and high boiling oils in these still tails. These residues and oils pass through heat exchangers before discharging to the treatment plant.

Butanol oils, and other by-products with boiling points between those of ethanol and water, are removed from the sides of the stills and sent through a condenser. Enough water is added to this crude mixture (ethanol, water, and by-products) to maintain a desired gravity. The ethanol-water layer is withdrawn by pumps and sent to the top of the acetaldehyde scrubber as scrubbing liquid. The oil layer is periodically withdrawn for butanol recovery.

2. Acetaldehyde Conversion

The acetaldehyde conversion system consists of three converters, operating in parallel and heated by circulating liquid Dowtherm, a heat exchanger, partial condenser, vapor compressors, second condenser, and gas scrubber column.

Ethanol vapor from the top of the high-pressure ethanol stills is fed through a heat exchanger where it is superheated and passed to the acetaldehyde converters. Flow rates are manually controlled. Converter outlet gases pass back through a heat exchanger supplying heat for incoming feed, and then pass into a partial condenser. Pressure is automatically controlled. Condensate (ethanol, water, and acetaldehyde) collects in a receiver, and the vapors not condensed pass through entrainment separators to acetaldehyde vapor compressors where they are compressed. From the compressors the vapors pass through a second condenser into the base of the acetaldehyde scrubber where the remaining acetaldehyde and ethanol vapors are absorbed by process water and the water layer from the decanter for the side stream from the ethanol stills. Hydrogen passes off the top of the column and is sent to the fuel gas system.

Condensate from the receiver is sent by pump, partly overhead, to the top of the butadiene scrubber (mentioned later in butadiene conversion), with the remainder joining the residues from the acetaldehyde scrubber to the acetaldehyde still. The combined flow consists of acetaldehyde, ethanol, water, and by-products. Acetaldehyde vapor is withdrawn from the top of the still and piped to the butadiene conversion system.

3. Butadiene Conversion

The butadiene conversion system consists of converters, heat exchangers in parallel, partial condensers in parallel, vapor compressors, a partial condenser, and gas scrubber columns.

A mixture of ethanol vapor (from high-pressure stills) and acetaldehyde vapor (from acetaldehyde still) is fed through parallel heat exchangers and then passed to butadiene converters. The flow of acetaldehyde is controlled by the pressure in the converter feed header, while the flow of alcohol is automatically controlled by a ratio flow controller, recording the amount of acetaldehyde. Converter outlet gases pass back through parallel heat exchangers, supplying heat for incoming feed and then pass into parallel partial condensers.

Condensate (acetaldehyde, oils, ethanol, water, butadiene, and other by-products) collects in the condensate receiver, and vapors not condensed are passed through entrainment separators and compressed. The compressed vapors then pass through another condenser into the base of the butadiene scrubber where the remaining butadiene is absorbed in acetaldehyde-alcohol liquid feed (liquid is partly from condensate receiver in acetaldehyde conversion system and partly from butadiene forecolumn tails). Gases, leaving the top of the butadiene scrubber, are saturated with materials of the liquid feed (acetaldehyde and alcohol) and these are removed in a gas scrubber with water. Gases (noncondensable, ethylene, propylene, and butadiene) pass from the top of the column to the fuel gas system. Residues from the base of the gas scrubber go to the oil extractor.

Liquid from the condensate receiver is pumped to join the residues from the butadiene scrubber in going to the crude butadiene storage tank. The combined flow consists of acetaldehyde, ether, ethanol, water, and butadiene. This storage tank furnishes the entire feed for the butadiene purification system.

4. Butadiene Purification System

Major processing steps involved in butadiene purification are: (1) stripping of crude butadiene from condensed liquids of butadiene conversion (performed by butadiene forecolumn), (2) removal of acetaldehyde from crude butadiene (performed by butadiene final product scrubber), and (3) removal of materials with boiling points in range of and below butadiene (performed by chlorex absorption system).

The butadiene forecolumn is heated by external, inclined calandrias. Feed is pumped through a preheater to the middle section of the column.

The overhead vapor consists of an azeotrope of butadiene and acetaldehyde, and small amounts of materials boiling in the range of and below butadiene. Most of the overhead vapor is refluxed. Residues from this column (acetaldehyde, ether, ethanol, and water) are used as the main feed to the by-product still (completely described later on, under Recovery Distillation System). Temperatures, liquid level, reflux, and feed, are automatically controlled.

Overhead vapor from the forecolumn goes directly to the base of the butadiene final product scrubber. Acetaldehyde is absorbed from incoming vapor with water. The scrubber tails are fed by pressure into the by-product still make-line. Flows and pressure are automatically controlled.

Acetaldehyde-free vapor of high butadiene content from the top of the final product scrubber enters the side of the butadiene absorber. This column is controlled by a pressure controller that regulates the amount of direct steam to the absorber. Liquid chlorex, pumped to the top of the absorber, preferentially absorbs butadiene from the incoming vapor and allows materials boiling in the range of, and below, butadiene to pass out the top of the column to the absorber recovery system. Chlorex feed, liquid level, and blowoff are automatically controlled.

Residues, consisting of absorbed butadiene, chlorex, and water, are pumped to a point near the top of the stripping still. This column is packed with Raschig rings, with steel gratings at intervals. Pressure, steam feed, and temperature are automatically controlled.

Overhead vapor (butadiene, water, and chlorex) is passed through a partial condenser where chlorex, water, and a small amount of butadiene are condensed and collected in a receiver. Receiver condensate is pumped to the top of the stripper still. Noncondensed buradiene vapors are compressed and discharged to the butadiene still.

Residues from the stripping still, containing water and chlorex, pass through an aftercooler to the chlorex decanter tank, where the chlorex forms a bottom layer and is re-used in the process. The top layer in the decanter tank, consisting of 98.9% water and 1.1% chlorex, is pumped to the chlorex recovery still. This is a column packed with steel Raschig rings and heated by direct steam. Its purpose is to strip the chlorex out of the water. All chlorex leaves the top of the column in a mixed chlorex-water vapor, which is condensed. The condensate joins the residues from the stripping still in going to the decanter. The tails from the recovery still are discharged to the sewer (dilute wastes) as a waste.

During use, the chlorex liquid develops traces of acidity, which are neutralized by adding a sufficient amount of caustic soda to the chlorex stream as it is pumped to the butadiene absorber. A small proportioning pump performs this duty.

5. Butadiene Refining System

Small traces of impurities in the butadiene produced in the purification system, are removed by final distillationin refining still columns. Pressures in this system are automatically controlled.

Noncondensed vapors from the chlorex stripping still are discharged to a tray of the first refining still. The overhead is condensed, with most of the condensate being refluxed, and the remainder pumped to tanks as finished product of high purity. The residue from this refining still is fed to a tray of another refining still. A fixed reflux ratio is held on this still, with the remainder going to pure product tanks. Residues from this still are fed to a tray of still another refining still. The remaining overhead goes back to a tray of the second still. Residues from the third still are periodically pumped to impure tanks. Relatively pure butadiene is inhibited with [redacted] tertiary butyl catechol and pumped to field storage.

A vapor side-stream is taken from a tray of the third refining still at butadiene unit number 3 and run through a countercurrent extractor packed with Raschig rings. Temperature-conditioned water washes the vapor stream and discharges to the sewer. The vapors are condensed and pumped to tanks. This washed product consists of butadiene, butene-2, and methyl ethyl ether.

6. Recovery Distillation System

The recovery distillation system performs the following functions: reconcentrates unreacted acetaldehyde and ethanol from the conversion systems, removes by-products from the process cycle, and furnishes acetaldehyde and ethanol vapor for the conversion systems. The distillation units of this system are continuous in operation, and operate more or less in series. The ethanol recovery still system has already been discussed in the Ethanol Still Section.

The acetaldehyde recovery system strips acetaldehyde from the acetaldehyde conversion system and feeds it to the butadiene conversion system. Feed from the acetaldehyde condensate receiver and acetaldehyde scrubber is pumped through a preheater to the middle section of the acetaldehyde still. Temperatures, pressures, feed, and reflux liquid level, are automatically controlled. Vapor from the top of the column containing a high percentage of acetaldehyde, and that for butadiene conversion, is withdrawn ahead of the condenser for the reflux system. The still residue (ethanol and water, by-products, and small amount of acetaldehyde not completely exhausted from the feed material) is fed into the base of the by-product still.

The primary purpose of the by-products recovery still system is to recover ethanol and acetaldehyde from various points in the butadiene process and re ycle them for butadiene production. It also recovers various by-products from water streams and diverts them to recovery systems or fuel utilization systems. This column is heated by external calandrias. Temperatures, pressures, feeds, and steam flow, are automatically controlled. Condensed overhead is refluxed. The feed is tails from the acetaldehyde still and the butadiene forecolumn.

Residues from the by-products column are fed to the low-pressure, ethanol recovery stills. The overhead vapors consist of various azeotropes involving acetaldehyde, water, ether, ethyl acetate, butraldehyde, ethanol, methyl ethyl ketone, and low-boiling hydrocarbon oils. To assist in the establishment of these azeotropes with water and to keep ethanol out of the vapor, water is added to the top of the column. The entire overhead is condensed, with part of the condensate being sent along with the butadiene final product scrubber tails, to the by-product decanter.

The liquids in the decanter separate into two layers, an acetaldehyde water layer on the bottom and an oil-acetaldehyde layer on the top. The bottom layer is pumped as feed to the acetaldehyde still, while the top layer decants by gravity to a tank. The oil layer in the tank is pumped, along with tails from the butadiene by-product gas scrubber, to an oil extractor. Oil, containing ether, acetaldehyde, and alcohol, decants to storage tanks. The extractor bottoms are pumped back to the by-product make decanter.

7. Ether Recovery

The oil extractor heads from each unit are fed to a batch utility still which is equipped with a steam-heated kettle. All components boiling at or lower than ether are stripped as overhead. The residual oil in the kettle is cooled and scrubbed with process water in an extractor filled with Raschig rings. The washed oil is pumped to another batch utility still, where ethyl acetate is separated and the residual oil goes to fuel. The water layer is held for alcohol recovery. The overhead is pumped to the batch utility still of another unit, where all four carbon organics, ether-acetaldehyde azeotrope, and lighter materials are stripped overhead. This overhead is scrubbed with process water in an extractor filled with Raschig rings for acetaldehyde removal. The water layer joins the tails from the final product butadiene scrubber for acetaldehyde recovery. The light hydrocarbon oil layer is pumped to a third batch utility still where four cuts (butadiene, methyl ethyl ether, acetaldehyde, and ether) are drawn off as overhead and the tails are pumped to fuel. The still tails from the second batch utility still are fed to ether storage or the last mentioned batch utility still for ether refining. The still residues from the latter still are used as fuel.

8. Blowoff Recovery System

The butylene blowoffs from the butadiene absorbers of all four units are collected in a header and fed to an absorber where butadiene and butylenes are absorbed with chlorex. Lighter hydrocarbons are stripped off for ethylene recovery. The column tails (butadiene, butylenes, chlorex and water) are fed to a stripping still where the butadiene and butylenes are stripped off by direct steam. Any chlorex condensed from the overhead is fed back as reflux. The still tails are cooled, pumped to a decanter, and the chlorex layer is recycled to the absorber.

WASTE SOURCES

The main uses of water in the butadiene plant are for cooling, and process operations. The cooling water is used indirectly, and consequently is discharged to the sewers relatively uncontaminated. Process water is used directly in the production units in the form of scrubbing water and heating steam. A certain amount of water is produced in the system as a chemical reaction and product. All process water must be removed from the product and is discharged along with small amounts of process products to waste.

There are two separate sewer systems in the butadiene area, the so-called contaminated system (concentrated wastes) and the uncontaminated system (relatively low concentrations of waste constituents).

9. Contaminated Wastes (Concentrated)

All of the relatively contaminated process water from the units is discharged to the contaminated waste system. These wastes from the process units are combined and charged to the ethanol stills for final recovery of ethanol. The high-pressure ethanol still tails then are discharged to the contaminated line which leads directly to the treatment system (described later in the waste section of the report). The average flow from three units, for the period of the survey, was 1.13 MGD. Approximately 40 per cent of the volume from the stills is fed into the stills in the form of direct steam for heating. If indirect heating could be used at this point, the volume of wastes might be reduced by 40 per cent.

10. Uncontaminated Wastes (Dilute)

Chlorex still tails, plus a small amount of wastes from tank pad, compressor, converter pad drainage, tank car washings and loading area drainage, plus cooler water, constitute the wastes going to this system. The bulk of the volume is represented by cooling water which, however, contains very little waste material. The chlorex still tails represent waste water from the chlorex recovery system. Chlorex from the butadiene stripping still contains the water which was introduced to the column as steam. This water is removed by decantation and is subjected to steam distillation in the chlorex still to remove dissolved chlorex. The volume of waste from one chlorex recovery still was approximately 0.034 MGD, whereas the total volume of uncontaminated waste, including chlorex still tails, was of the order of 20 MGD.

PRODUCTION

Approximately 2.3 lb of butadiene are produced per gallon of ethyl alcohol consumed. Each unit has several converters, and production varies directly with the number of converters in operation. Production also varies with the age of the catalysts; the newer the catalyst, the greater the production.

11. Raw Materials

The principal raw material is ethyl alcohol. Minor quantities of chlorex, sodium hydroxide, tertiary butyl catechol, Dowtherm and lime are also consumed.

12. Materials Produced

Butadiene is the major product. Rated production capacity is approximately 80 tons per day per unit. The principal by-products are ether, hydrogen, fuel gases, butanol, butylene-butene mixture, and fuel oil.

SURVEY PROCEDURES

13. Sample Collection

Butadiene operations are more or less continuous. It was assumed that waste flows were constant, and equal portions of samples were taken for compositing. Samples were collected at hourly intervals over 8-hour periods from 8:00 A.M. to 4:00 P.M. They were collected from the following points at the time of the survey:

	Source	Station
(1)	Ethanol still tails (combined flow from units #2, #3, and #4)	5-a
(2)	Chlorex still tails (composite of samples from units #2, #3, and #4)	13
(3)	North sewer (converter side) from unit #2, to uncontaminated sewer system	A-1
(4)	South sewer (still side) from unit #2, to uncontaminated sewer system	B-1
(5)	North sewer from unit #3	C-1
(6)	South sewer from unit #3	D-1
(7)	North sewer from unit #4	E-1
(8)	South sewer from unit #4	F-1

(See Figure C-1 and Figure C-2 for location of sampling points).

14. Flow Data

All flow data with the exception of that from the concentrated wastes line (Sta. 5-a) were estimated from water usage values based on orifice meter records. An orifice plate meter furnished direct flow data for the concentrated wastes flowing to treatment.

15. Laboratory Analyses

The following laboratory determinations were made on samples collected from this plant area:

(1) Threshold odor number (hot and cold).

(2) pO (hot and cold) - Calculated from threshold odor number values. Fractional, rather than whole, numbers used to point out small differences.

(3) Oxygen consumed from dichromate.

(4) B.O.D., 5-day.

(5) pH.

The procedures followed in making threshold odor number, B.O.D. and pH determinations were those given in "Standard Methods for the Examination of Water and Sewage," 9th edition.(1) The dilution technique for threshold odor was not followed. Successive dilution ratios, with odor-free water, of 2:1 were used in order to conform to the physiological Weber-Fechner law, that is, each successive dilution was 1/2 that of the previous one. The procedure for pO values was according to the 8th edition of "Standard Methods for the Examination of Water and Sewage." The procedure for the oxygen consumed from dichromate determination is given in the final appendix at the end of this report.

16. Explanation of Laboratory Analyses

A brief explanation of the various laboratory determinations is given in the appendix at the end of this report and is intended to serve as an aid in the interpretation of the analytical results reported.

DISCUSSION OF RESULTS

Butadiene plant operations were normal during the period of the survey. Three of the four units (#2, #3, and #4) were in operation. Unit #4 was put on stream the week previous to the beginning of the survey. Starting operations are variable, and this may account for the relatively high threshold odor data obtained from south sewer samples of unit #4.

Daily analytical results and quantities of waste constituents will be found in Table A-1 in the appendix of this section of the report.

17. Contaminated Wastes

These waste represent the relatively concentrated wastes discharged from the butadiene plant. The tails from the high-pressure ethanol stills constitute all of these wastes.

The daily average gross and net concentrations and quantities of waste constituents discharged from the butadiene plant to treatment facilities, during the period of the survey, are as follows:

Waste Constituents	Quantities				
	Gross (1)				
	Maximum	Minimum	Average	Raw Water	Net (2)
Threshold odor number:					
Cold	256,000	4,000	23,000 (3)	13	23,000
Hot	256,000	8,000	56,600 (3)	12	56,600
pO:					
Cold	18	12	14.5	4.6	14.5
Hot	18	13	15.8	4.5	15.8
Weighted threshold odor (4):					
Cold	249,000	3,920	22,500	13	22,500
Hot	249,000	7,840	55,500	12	55,500
Oxygen consumed ($K_2Cr_2O_7$):					
Concentration, ppm	10,800	6,340	9,050	24	9,030
Quantities, lbs/day	85,100	51,800	73,800	200	73,600
B.O.D., 5-day:					
Concentrations, ppm	6,080	3,570	4,700	2	4,700
Quantities, lbs/day	47,800	29,100	38,300	16	38,300

Average daily flow = 0.98 MGD

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(1) Gross values shown are in all cases the average values of individual samples as shown in Table A-1. The products of average flows and average concentrations do not necessarily equal the values shown.

(2) Net pO values are calculated from daily net pO values.

(3) Average threshold odor values are geometric means (correspond to average pO).

(4) Weighted odor values are product of odor value and flow in millions of gallons per day.

All of the so-called contaminated wastes are discharged to the treatment system which will be discussed in a later section (C).

The residues from the ethanol stills contain 0.3 to 0.5 per cent acetic acid and this fact is reflected in the relatively low pH values of the wastes. The ratio of average oxygen consumed from dichromate concentrations to average 5-day B.O.D. concentrations is 1.9 to 1.

18. Uncontaminated Wastes

These wastes include all wastes considered too dilute for treatment. Each butadiene unit has two uncontaminated sewer systems, one for the still area and the other for the converter area. All of these wastes flow to the main outfall.

The daily average, gross and net concentrations and quantities of waste constituents discharged in this system are shown in Table A-2.

The north sewer from each butadiene unit represents the converter side, while the south sewer represents the still side. The wastes from the still side of butadiene unit #4 were sampled over two different periods and the odor values were relatively high on both occasions. This may be explained by the fact that this unit had just been put into operation.

The chlorex still tails were the only individual wastes sampled in this waste system. The average oxygen consumed from dichromate concentrations were relatively high. The ratio of average oxygen consumed concentration to average 5-day B.O.D. concentration was 28 to 1.

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Table A-2 - Daily Average Gross (1) and Net, Concentrations and Quantities of Waste Constituents, Uncontaminated Waste System of Butadiene Plant

	Flow MGD	Threshold Odor Number (4) Cold	Threshold Odor Number (4) Hot	pO (2) Cold	pO (2) Hot	Weighted Odor (Threshold) Cold	Weighted Odor (Threshold) Hot	Oxygen Consumed ($K_2Cr_2O_7$) ppm	Oxygen Consumed ($K_2Cr_2O_7$) lb/day	5-day B.O.D. ppm	5-day B.O.D. lb/day	pH
Butadiene Unit #2, North Sewer, Manhole #8, Sampling Point #A-1												
Gross	7.38	56		5.8		410		46	2,830	5	310	6.5 - 6.6
Raw Water(3)		45		5.5		330		39	2,370	3	180	6.4 - 7.2
Net		11		3.1		80		7	460	2	130	
Butadiene Unit #2, South Sewer, Manhole #10, Sampling Point #B-1												
Gross	16.9	240		7.8		4,140		38	5,340	12	1,720	6.3 - 6.4
Raw water(3)		45		5.5		760		39	5,410	3	420	6.4 - 7.2
Net		195		7.6		3,380				9	1,300	
Butadiene Unit #3, North Sewer, Manhole #27, Sampling Point #C-1												
Gross	6.19	110		6.8		680		49	2,540	7	360	6.4 - 6.6
Raw Water(3)		45		5.5		280		39	1,980	3	160	6.4 - 7.2
Net		65		5.4		400		10	660	4	200	
Butadiene Unit #3, South Sewer, Manhole #29, Sampling Point #D-1												
Gross	14.7	330		8.3		4,820		46	5,580	12	1,470	5.6 - 6.4
Raw water(3)		45		5.5		660		39	4,710	3	370	6.4 - 7.2
Net		285		8.1		4,160		7	870	9	1,100	
Butadiene Unit #4, North Sewer, Manhole #44, Sampling Point No. E-1												
Gross	5.62	160		7.3		900		45	2,110	5.8	270	5.7
Raw Water(3)		10		5.5		250		39	1,800	3.0	140	6.4 - 7.2
Net		150		7.2		840		6	310	2.8	130	
Butadiene Unit #4, South Sewer, Manhole No. 47, Sampling Point #F-1												
Gross	12.9	2700	1500	11.4	10.6	35000	20,400	55	6,200	13	1350	5.8 - 6.4
Raw water(3)		25	12	4.6	3.5	320	150	26	2,800	3.3	360	[illegible].2 - 7.2
Net		2675	1488	11.4	10.6	34680	20,200	29	3,400	9.7	990	
Chlorex Still Tails, Sampling Point #13, Composite from Buta Units No.2, 3, and 4												
Gross	0.102	68	140	6	7.1	6.9	14.	430	370	16	14	9.9 - 10.1
Raw Water(3)		48	72	5	6.1	4.8	7.2	12	10	1	1	6.7
Net		20	68	5	6.2	2.1	6.8	420	360	15	13	

(1) Gross values shown are in all cases the average values of individual samples as shown in Table A-1. The products of average flows and average concentrations do not necessarily equal the values shown.

(2) All pO values are calculated from corresponding threshold odor values. Average net values are average values obtained from daily net values.

(3) The raw water values are based on average waste constituent concentrations for the particular days the wastes were sampled.

(4) Average threshold odor values are geometric means.

SUMMARY

Based on analytical data obtained during this survey, the total volumes and net quantities of waste constituents discharged from three operating units (#2, #3, and #4) of the butadiene plant to treating facilities or to sewers, are as follows:

	Contaminated Wastes	Uncontaminated Wastes	Total
Volume, MGD	0.98	63.69	64.67
Weighted threshold odor (cold)(1)	22,500	43,500	66,000
Oxygen consumed ($K_2Cr_2O_7$), lbs/day	73,600	5,700	79,300
B.O.D., 5-day, lbs/day	38,300	3,850	42,150

(1) Empirical values obtained by multiplying odor concentrations by volumes in millions of gallons per day.

The percentages of total wastes discharged from each system are as follows:

	Contaminated Wastes (1)	Uncontaminated Wastes
Volume	1.5	98.5
Weighted threshold odor (cold)	34	66
Oxygen consumed ($K_2Cr_2O_7$)	93	7
B.O.D., 5-day	91	9

(1) These wastes are sent to treatment. See discussion of waste treatment in Section C, page 98.

Using a butadiene production value of 75 tons per unit per day, the unit volumes of wastes and unit net quantities of waste constituents per tonof butadiene produced are as follows:

Waste System	Unit Volumes and Quantities			
		Quantities per Ton Product		
	Volume per Ton Product	Weighted Threshold Odor (Cold)	Oxygen Consumed ($K_2Cr_2O_7$)	B.O.D. 5-day
	gal		lb	lb
Contaminated	4,350	100	327	170
Uncontaminated	283,000	194	25	17
Total	287,350	294	352	187

TABLE A-1 SUMMARY OF DAILY ANALYSES

CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS

BUTADIENE PLANT

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Date 1952	Flow MGD	Threshold Odor Number		pO		Weighted Odor (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-Day B.O.D.		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	
BUTADIENE UNIT NO.2, NORTH SEWER, EAST BRANCH, MANHOLE NO.8 - SAMPLING POINT NO. A1 8 hour composite (increment each hour)												
May 20	7.63	40	-	5.3	-	305	-	48.4	3076	4.70	299	6.5
May 21	7.13	80	-	6.3	-	570	-	43.6	2590	5.26	312	6.6
Average	7.38	56	-	5.8	-	410	-	46	2830	5.0	310	
BUTADIENE UNIT NO. 2, SOUTH SEWER, EAST BRANCH, MANHOLE NO. 10 - SAMPLING POINT NO.B1 8 hour composite (increment each hour)												
May 20	17.98	320	-	8.3	-	5754	-	34.3	5137	13.0	1947	6.4
May 21	15.78	160	-	7.3	-	2524	-	42.2	5547	11.4	1498	6.3
Average	16.88	240	-	7.8	-	4140	-	38	5340	12	1720	
BUTADIENE UNIT NO. 3, NORTH SEWER, WEST BRANCH, MANHOLE NO.27 - SAMPLING POINT NO.C1 8 hour composite (increment each hour)												
May 20	6.25	320	-	8.3	-	2000	-	43.6	2270	9.20	479	6.6
May 21	6.13	40	-	5.3	-	245	-	55.1	2810	4.81	246	6.4
Average	6.19	110	-	6.8	-	680	-	49	2540	7.00	360	
BUTADIENE UNIT NO. 3, SOUTH SEWER, WEST BRANCH, MANHOLD NO.29 - SAMPLING POINT NO.D1 8 hour composite (increment each hour)												
May 20	14.73	640	-	9.3	-	9427	-	43.2	5300	12.2	1497	6.4
May 21	14.45	160	-	7.3	-	2312	-	48.7	5860	12.0	1444	5.6
Average	14.59	330	-	8.3	-	4820	-	46	5580	12	1470	
BUTADIENE UNIT NO. 4, NORTH SEWER, WEST BRANCH, MANHOLE NO.44 - SAMPLING POINT NO.E1 4 hour composite (increment each hour)												
May 21	5.62	160	-	7.3	-	899	-	45.0	2107	5.76	270	5.7

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TABLE A-1 SUMMARY OF DAILY ANALYSES Cont'd-2

CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS

BUTADIENE PLANT

Date 1952	Flow MGD	Threshold Odor Number Cold	Threshold Odor Number Hot	pH Cold	pH Hot	Weighted Odor (Threshold) Cold	Weighted Odor (Threshold) Hot	O_2 Consumed $K_2Cr_2O_7$ ppm	O_2 Consumed $K_2Cr_2O_7$ lb/day	5-day B.O.D. ppm	5-day B.O.D. lb/day	pH
BUTADIENE UNIT NO.4, SOUTH SEWER, WEST BRANCH, MANHOLE NO.47 - SAMPLING POINT NO.F1 8 hour composite (increment each hour)												
May 20	12.97	5120	-	12.3	-	66,400	-	70.1	7570	9.4	1016	6.4
May 21	13.24	2560	-	11.3	-	33,890	-	72.0	7940	9.3	1026	6.2
June 16	12.39	1600	1600	10.6	10.6	19,820	19,820	30.4	3938	14.1	1455	6.1
June 17	13.17	3200	1600	11.6	10.6	42,140	21,070	48.8	5354	17.4	1909	5.8
Average	12.94	2700	1500	11.4	10.6	35,000	19,400	55	6200	13	1350	5.8-6.4
CLOREX STILL TAILS - BUTADIENE PLANT - SAMPLING POINT NO.13 (Composite from Units #2, #3, #4) 8 hour composite (increment each hour from each still)												
June 18	0.10	100	100	6.6	6.6	10	10	429	370	15.7	13	9.9
June 19	0.10	50	200	5.6	7.6	5	20	428	360	15.9	14	10.1
Average	0.10	68	140	6.1	7.1	6.9	14	430	370	16	14	-
TOTAL OIL SKIMMER INFLUENT - SAMPLING POINT NO. 5 24 hour composite (increment each hour)												
May												
14-15	1.532	8000	-	13	-	12,256	-	6350	81036	2820	35988	3.5
15-16	1.522	$1x10^{12}$(1)	-	40(1)	-	$1.5x10^{12}$(1)	-	7644	96913	2545	32266	3.6
18-19	1.546	250,000	-	18	-	386,500	-	7820	100,707	2760	35544	3.5
19-20	1.531	50,000	-	15.6	-	76,550	-	9584	122,227	3555	45378	4.3
25-26	1.463	10,000	-	13.3	-	14,630	-	10175	124,000	4588	55913	3.8
26-27	1.484	20,000	-	14.3	-	29,680	-	10494	129,724	4729	58458	3.9
27-28	1.474	256,000	256,000	18	18	377,344	377,344	10286	126,296	3697	45390	3.6
8 hour composite (increment each hour)												
28	1.571	16,000	16,000	14	14	25,136	25,136	-	-	3990	52215	3.2
Average	1.52	49,300	65,000	15.6	16	75,000	98,800	8910	111,600	3590	45100	-

(1) Not included in average value

Chemical Division
Koppers Company
Kobuta, Pennsylvania

TABLE A-1 SUMMARY OF DAILY ANALYSES Cont'd-3
CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS
BUTADIENE PLANT

Date 1952	Flow MGD	Threshold Odor Number		DO		Weighted Odor (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-Day B.O.D.		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	
BUTADIENE WASTE TO OIL SKIMMER - SAMPLING POINT NO. 5a 8 hour composite (increment each hour)												
June 9	0.974	256,000	256,000	18	18	249,344	249,344	9459	76,745	3880	31,480	3.9
June 10	0.943	16,000	128,000	14	17	15,088	120,704	10834	85,103	6080	47,760	3.8
June 11	0.980	4,000	8,000	12	13	3,920	7,840	6345	51,797	3570	29,143	4.0
June 12	1.023	16,000	32,000	14	15	16,368	32,736	9578	81,620	5260	44,824	3.8
Average	0.980	23,000	56,600	14.5	15.8	22,500	55,500	9050	73,800	4700	38,300	-

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SECTION B - STYRENE PRODUCTION OPERATIONS AND WASTES

Styrene is one of the two chemical compounds which copolymerize to form the base component GR-S synthetic rubber. The demands of the synthetic rubber program, brought about by the entry of the United States into World War II, made necessary a great increase in the production of styrene. At the beginning of the war, only one plant, the Dow plant at Midland, Michigan, produced styrene commercially. The Koppers Company plant at Kobuta, Pennsylvania, was built during World War II to provide styrene and butadiene for the synthetic rubber program.

Styrene monomer, also known as vinylbenzene, phenylethylene, or cinnamene, is a colorless liquid at ordinary temperatures and pressures, has a specific gravity of 0.907 at 20°C, and at atmospheric pressure has a boiling point of 146°C. Styrene monomer polymerizes rapidly at elevated temperatures, the rate of polymerization increasing almost logarithmically from 0.1 per cent per hour at about 60°C to greater than 40 per cent per hour at 130°C.

DESCRIPTION OF PROCESS

Basically, the process employed at Kobuta consists of the production and purification of ethylene, the purification of benzene, the alkylation of benzene with ethylene to produce ethylbenzene, the dehydrogenation of ethylbenzene to produce styrene, and the purification of product styrene. Discussion of each of these processes follows.

Figure B-1 is a diagram of the styrene plant showing the process waste system and indicating the waste streams sampled during the study.

1. Benzene Purification Process

At the present time, motor fuel and light oil, materials obtained by the destructive distillation of coal in by-product coke ovens, serve as a source of benzene for the Kobuta plant operation. In the benzene plant, benzene is separated from these mixtures and purified to a grade acceptable for subsequent alkylation to ethylbenzene.

Motor fuel and/or light oil from storage are charged to a forerunnings column. In this column the undesirable low-boiling compounds, or forerunnings, are removed from the mixture. The benzene-rich forerunnings still bottoms are charged to a "thiophene" still which produces a benzene-toluene-xylene overhead mixture.

The overhead benzene-toluene-xylene mixture from the thiophene column is condensed, passed through a water separator, and charged to an agitator for acid washing. The acid wash with sulfuric acid removes

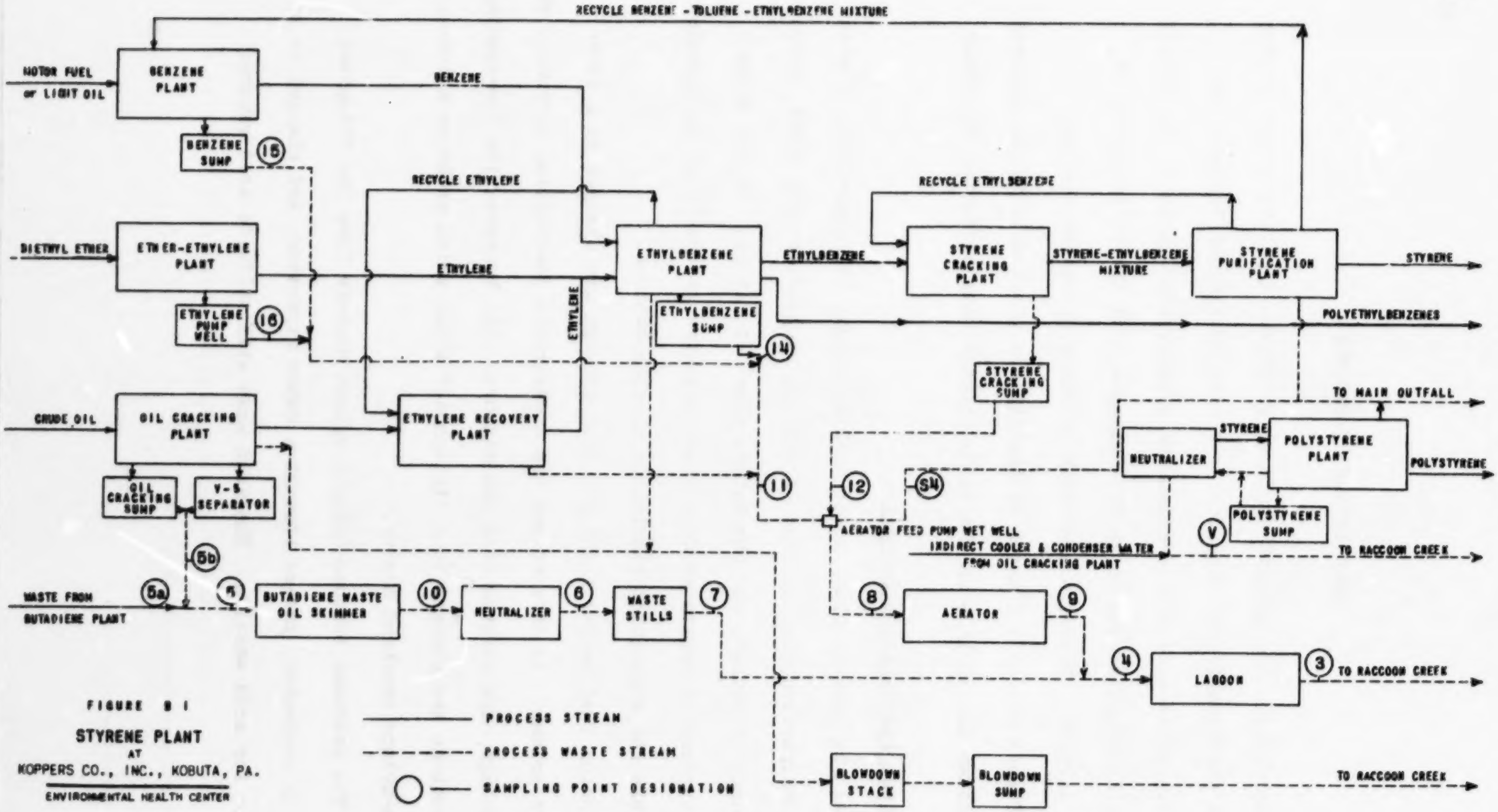
RECYCLE BENZENE - TOLUENE - ETHYLBENZENE MIXTURE
MOTOR FUEL or LIGHT OIL
BENZENE PLANT
BENZENE
BENZENE SUMP
15
RECYCLE ETHYLENE
RECYCLE ETHYLBENZENE
DIETHYL ETHER
ETHER-ETHYLENE PLANT
ETHYLENE
ETHYLBENZENE PLANT
ETHYLBENZENE
STYRENE CRACKING PLANT
STYRENE-ETHYLBENZENE MIXTURE
STYRENE PURIFICATION PLANT
STYRENE
ETHYLENE PUMP WELL
16
ETHYLENE
ETHYLBENZENE SUMP
14
POLYETHYLBENZENES
STYRENE CRACKING SUMP
TO MAIN OUTFALL
CRUDE OIL
OIL CRACKING PLANT
ETHYLENE RECOVERY PLANT
NEUTRALIZER
STYRENE
POLYSTYRENE PLANT
POLYSTYRENE
OIL CRACKING SUMP
V-5 SEPARATOR
11
12
S4
AERATOR FEED PUMP WET WELL
POLYSTYRENE SUMP
V
INDIRECT COOLER & CONDENSER WATER FROM OIL CRACKING PLANT
TO RACCOON CREEK
5b
WASTE FROM BUTADIENE PLANT
5a
5
BUTADIENE WASTE OIL SKIMMER
10
NEUTRALIZER
6
WASTE STILLS
7
8
AERATOR
9
4
LAGOON
3
TO RACCOON CREEK
PROCESS STREAM
PROCESS WASTE STREAM
SAMPLING POINT DESIGNATION
BLOWDOWN STACK
BLOWDOWN SUMP
TO RACCOON CREEK

FIGURE B 1

STYRENE PLANT
AT
KOPPERS CO., INC., KOBUTA, PA.

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unsaturated and sulfur-containing organic compounds. The acid sludge is separated, withdrawn from the agitator, and disposed of to an earth dump. Following the acid wash the mixture of benzene, toluene and xylene is neutralized in the agitator with caustic solution. The caustic sludge is withdrawn and disposed of in the same manner as the acid sludge.

The acid-washed benzol mixture is fed to a benzene column which produces an overhead stream of nitration grade benzene. This benzene stream is condensed, passed through a water separator, and sent to storage for feed to the ethylbenzene plant. The bottom fraction from this column is a mixture of toluene, xylene, benzene, and higher-boiling compounds. It is fed to a "toluene-xylene" still from which benzene, toluene, and xylene are withdrawn in order as overhead products. These streams are condensed, passed through a water separator, and sent to storage for subsequent use in the process or for market.

Liquid process wastes from the benzene plant consist of floor drainage, and separator water from the forerunnings column, the thiophene column, the benzene column, and the toluene-xylene column. These wastes pass through a benzene plant oil intercepting sump, the water phase from which is pumped to the aerator feed pump wet well for treatment in the aerator.

In the benzene plant some 2.1 million gallons per day of service water is used as a cooling medium in indirect coolers and condensers. This water is discharged to the main outfall sewerage system.

Figure B-2 is a simplified flow diagram representing the benzene purification process.

2. Ethylene Production and Purification

A. Ether-Ethylene Process - Ethylene may be produced by the dehydration of diethyl ether according to the following equation:

$$H_5C_2OC_2H_5 \xrightarrow[\text{catalyst}]{\text{heat}} 2C_2H_4 + H_2O$$

A number of factors, including temperature, pressure, charging rates, and choice of catalyst, affect conversion rates, ultimate yields, and the magnitudes of side reactions.

Ethyl alcohol, by similar reaction and under similar conditions, will also produce ethylene:

$$C_2H_5OH \xrightarrow[\text{catalyst}]{\text{heat}} C_2H_4 + H_2O$$

Diethyl ether is the primary feed stock now in use at the Kobuta plant for the production of ethylene by dehydration. In addition to ethylene, small amounts of hydrogen, certain paraffins, olefins, aldehydes and acids are produced by the process.

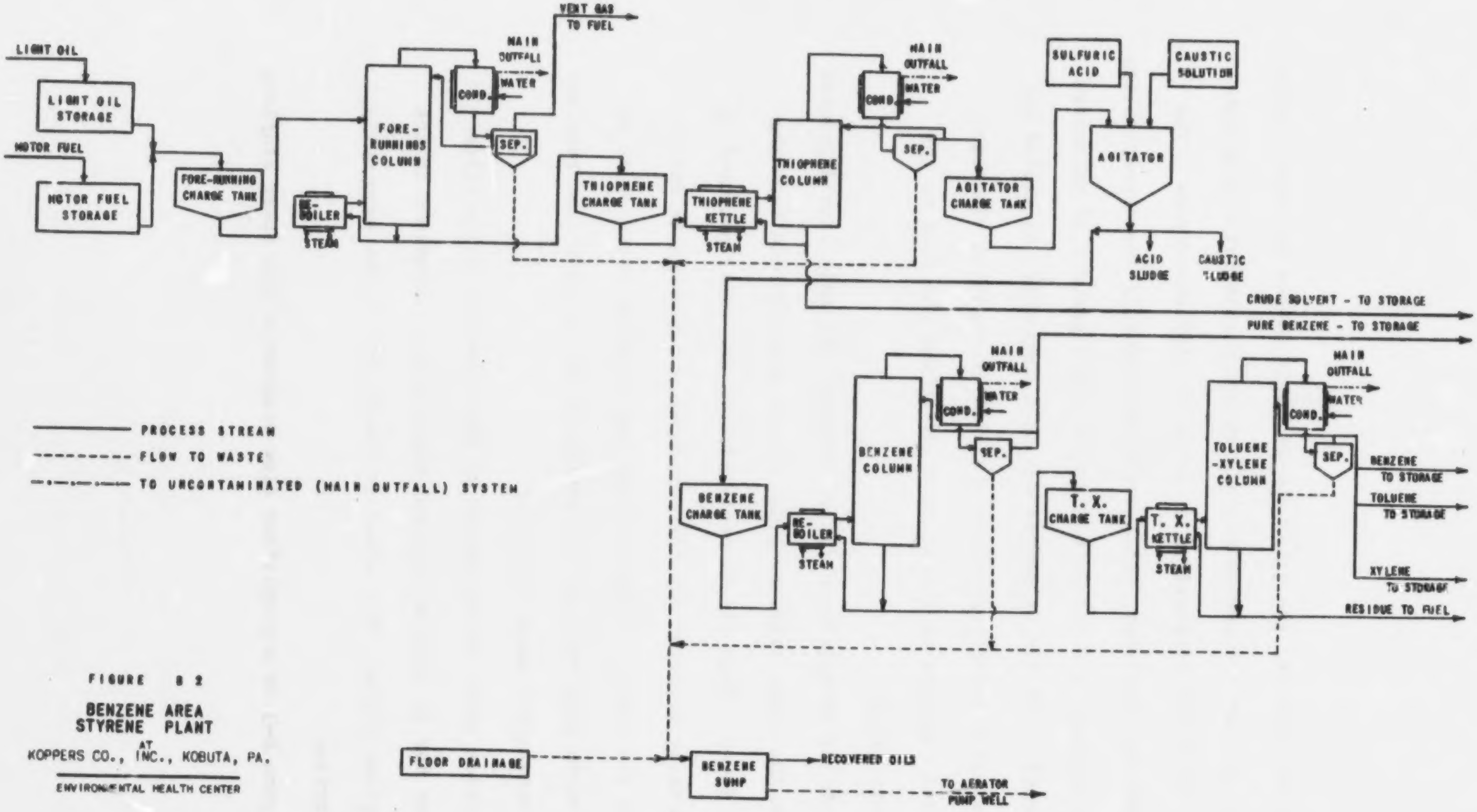
LIGHT OIL
LIGHT OIL STORAGE
MOTOR FUEL
MOTOR FUEL STORAGE
FORE-RUNNING CHARGE TANK
RE-BOILER
STEAM
FORE-RUNNING COLUMN
COND.
MAIN OUTFALL
WATER
SEP.
VENT GAS TO FUEL
THIOPHENE CHARGE TANK
THIOPHENE KETTLE
STEAM
THIOPHENE COLUMN
COND.
MAIN OUTFALL
WATER
SEP.
AGITATOR CHARGE TANK
SULFURIC ACID
CAUSTIC SOLUTION
AGITATOR
ACID SLUDGE
CAUSTIC SLUDGE
CRUDE SOLVENT - TO STORAGE
PURE BENZENE - TO STORAGE
BENZENE CHARGE TANK
RE-BOILER
STEAM
BENZENE COLUMN
COND.
MAIN OUTFALL
WATER
SEP.
T. X. CHARGE TANK
T. X. KETTLE
STEAM
TOLUENE -XYLENE COLUMN
COND.
MAIN OUTFALL
WATER
SEP.
BENZENE TO STORAGE
TOLUENE TO STORAGE
XYLENE TO STORAGE
RESIDUE TO FUEL
PROCESS STREAM
FLOW TO WASTE
TO UNCONTAMINATED (MAIN OUTFALL) SYSTEM
FLOOR DRAINAGE
BENZENE SUMP
RECOVERED OILS
TO AERATOR PUMP WELL

FIGURE 8 2

BENZENE AREA
STYRENE PLANT
AT
KOPPERS CO., INC., KOBUTA, PA.

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In the process, the ether charge stock passes through a vaporizer, then through a superheater, and enters a catalyst-filled converter in which the dehydration of ether to ethylene occurs. The stream from the converter, which contains primarily the decomposition products, ethylene and water, along with small amounts of unreacted ether, paraffin, olefin, aldehyde and acid compounds, is cooled and passed through a scrubbing column where it is scrubbed with water. The scrubbed ethylene is stored in a gas holder for feed to the ethylbenzene plant.

With the exception of floor drainage, the only liquid process waste from the ether ethylene plant is the water stream from the scrubbing tower. This stream contains both the water produced by the dehydration reaction and the scrubbing water which is introduced into the tower. Floor drainage and scrubber water go to an ethylene waste pump well and are pumped to the aerator feed pump wet well for subsequent waste treatment.

Service water in the amount of approximately 2.1 million gallons per day is used in indirect coolers and condensers in the ether ethylene plant. This water is discharged to the main outfall sewerage system.

Figure B-3 is a simplified flow diagram of the ether ethylene process.

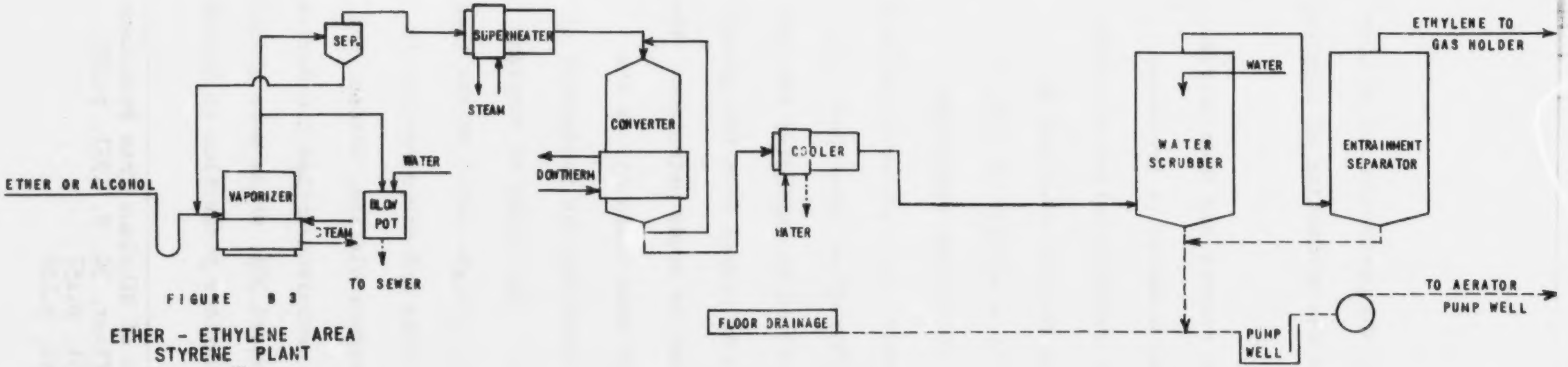
ETHER OR ALCOHOL
VAPORIZER
STEAM
SEP.
BLOW POT
WATER
TO SEWER
SUPERHEATER
STEAM
CONVERTER
DOWTHERM
COOLER
WATER
WATER SCRUBBER
WATER
ENTRAINMENT SEPARATOR
ETHYLENE TO GAS HOLDER
FLOOR DRAINAGE
PUMP WELL
TO AERATOR PUMP WELL

FIGURE B 3

ETHER - ETHYLENE AREA
STYRENE PLANT
AT
KOPPERS CO., INC., KOBUTA, PA.

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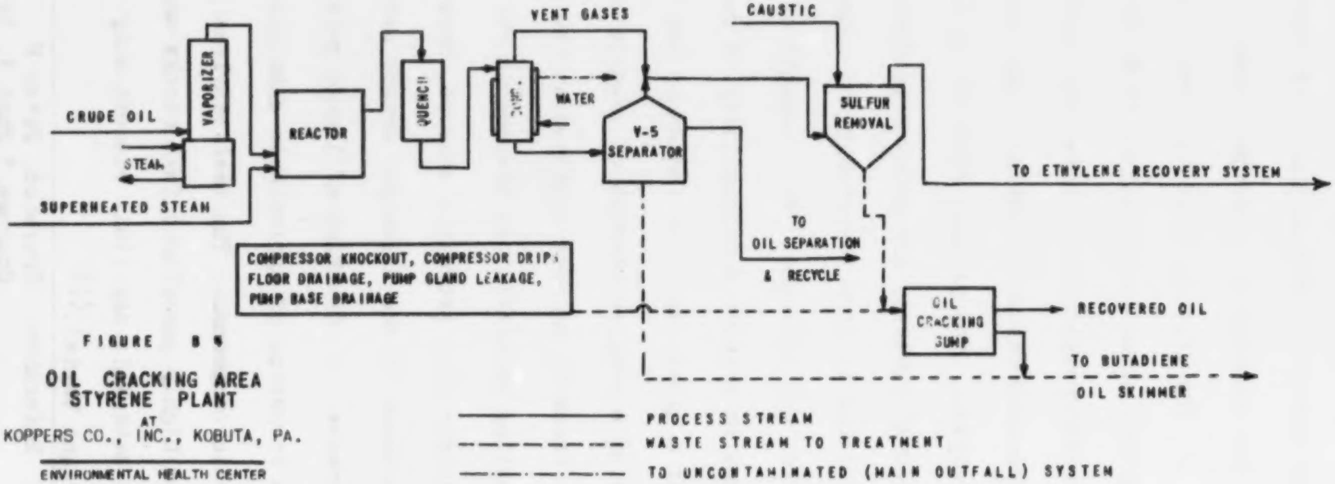
CRUDE OIL
VAPORIZER
STEAM
SUPERHEATED STEAM
REACTOR
QUENCH
VENT GASES
WATER
V-5 SEPARATOR
CAUSTIC
SULFUR REMOVAL
TO ETHYLENE RECOVERY SYSTEM
TO OIL SEPARATION & RECYCLE
COMPRESSOR KNOCKOUT, COMPRESSOR DRIP, FLOOR DRAINAGE, PUMP GLAND LEAKAGE, PUMP BASE DRAINAGE
OIL CRACKING SUMP
RECOVERED OIL
TO BUTADIENE OIL SKIMMER
PROCESS STREAM
WASTE STREAM TO TREATMENT
TO UNCONTAMINATED (MAIN OUTFALL) SYSTEM

FIGURE B 4

OIL CRACKING AREA
STYRENE PLANT
AT
KOPPERS CO., INC., KOBUTA, PA.

ENVIRONMENTAL HEALTH CENTER

B. Oil Cracking Process - In addition to the production of ethylene from ether, the Kobuta plant operates a unit for the production of ethylene by the cracking of crude petroleum.

The production of ethylene from petroleum sources has been increased manyfold since the beginning of World War II, and a number of processes for its accomplishment have been developed. The dehydrogenation of ethane represents the most simple of the reactions which produce ethylene by pyrolysis. The primary reaction is accompanied by a minimum of side reactions; however, the primary products continue to undergo secondary reactions to form acetylenic and aromatic compounds, and eventually methane, carbon and hydrogen. This example of the pyrolysis of an ideal pure compound to produce a multiplicity of compounds is cited to emphasize the fact that a great number of compounds may be expected to result from the pyrolysis of a complex mixture of organic compounds such as crude petroleum. The oil cracking process employed at the Kobuta plant uses crude oil as the starting material. In his series of articles concerning the production of ethylene from petroleum sources, Sherwood states: "The yield of ethylene decreases as the molecular weight and the carbon/hydrogen ratio of the feed increase ... Cracking of liquid petroleum fractions and crude results in the formation of appreciable quantities of by-product olefins, dienes, and cyclic compounds. The best ethylene yields from petroleum crudes are derived from highly paraffinic feed stocks and do not exceed 30%, while more aromatic raw materials may limit economically feasible ethylene production to 12-15% (weight basis).(1)

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(1) Reference: Sherwood, Peter W., "Production of Ethylene from Petroleum Sources," Part I, Petroleum Refiner, 30, 9, 1951, p.220.
Part II, Ibid 30, 11, 1951, p.157.
Part III, Ibid 31, 1, 1952, p.126.

In the process employed at the Kobuta Plant, crude oil is first partially vaporized and fed into a reactor. The reactor is maintained at high temperature, and pyrolysis of some components of the crude oil results in the production of numerous new compounds, among which is included ethylene. The mixture leaving the reactor is immediately quenched to minimize the continuation of reaction, polymerization, and condensation. Following the quenching operation, the mixture is condensed and cooled, then enters an enclosed separator in which the oil, water and gas phases separate by gravity. The oil phase goes from the separator to an oil separation and recycle system. The water phase goes to the butadiene waste oil skimmer. The ethylene-bearing gas stream is passed through caustic solution for the removal of sulfur compounds. Spent caustic solution discharges to the oil cracking gravity type oil-water separator.

The sweetened gas stream is processed to produce a stream of ethylene and higher-boiling components. This gas stream is the feed material for the ethylene recovery plant.

Liquid process wastes from this plant include the water stream from the process oil-water separator which receives the cracked product and the water stream from the oil cracking plant gravity type oil-water separator which receives compressor knockout, compressor drips, floor drainage, pump gland leakage, pump base drainage, and spent caustic from the product gas sweetening operation. The water phase from both of these separators is pumped to the butadiene waste oil skimmer.

Approximately 7.8 million gallons per day of service water is used in indirect coolers and condensers in the oil cracking plant. This water is discharged to Raccoon Creek.

Figure B-4 is a simplified flow diagram which represents the oil cracking process.

C. Ethylene Recovery Process - The Kobuta plant employs a low temperature fractionation method for the separation of ethylene from the mixture of gases produced in the oil cracking plant. The dried gases are cooled to a very low temperature and liquefied in a series of precoolers, then are fed to a demethanizer column. The overhead stream from this column contains methane, hydrogen, and any other similarly light gases present. This stream is sent to the plant's fuel system. The bottom stream contains ethylene, ethane, acetylene, and the higher boiling hydrocarbons present in the feed mixture. This stream is sent to the ethylene column which produces an overhead stream of ethylene and a bottoms stream of ethane and higher boiling hydrocarbons.

The ethylene stream is sent through an absorption column in which an appropriate liquid solvent selectively absorbs acetylene while permitting the ethylene to pass through the column. Following the solvent scrubbing operation, the ethylene stream is water-scrubbed and is charged to the ethylbenzene process.

Acetylene-rich solvent from the ethylene gas solvent scrubber is charged to a solvent recovery column. This column produces an overhead stream of acetylene and a bottoms stream of stripped solvent which is cooled and re-used in the scrubber.

Bottoms from the water scrubber for the ethylene are charged to a solvent recovery column. Overhead from this column is cooled and returned to the solvent system. Column tails are recycled as feed to the ethylene scrubber with any in excess of needs being discharged to the contaminated waste system for treatment.

Liquid process wastes from the ethylene recovery plant include scrubbing water from the ethylene gas scrubber after steam stripping in a solvent recovery column, compressor knock-out, pump drips, and floor drainage. These wastes are pumped to the aerator feed pump wet well.

Approximately 0.46 million gallons of service water used in indirect coolers and condensers is discharged daily from this plant to the main outfall sewage system.

Figure B-5 is a simplified flow diagram which represents the ethylene recovery process.

3. Ethylbenzene Process

In the ethylbenzene plant, benzene and ethylene are reacted catalytically to produce ethylbenzene. The desired reaction is represented by the following equation:

$$C_6H_6+C_2H_4 \xrightarrow[\text{Catalyst}]{\text{Heat-pressure}} C_6H_5.C_2H_5$$

Accompanying the production of ethylbenzene is the formation of polyethylbenzenes.

Ethylene and benzene, under pressure, are passed through a preheating furnace, then are introduced into a catalyst-filled reactor where the alkylation reaction occurs. The reactor product stream, containing benzene, ethylbenzene, polyethylbenzenes, and a small amount of ethylene, is introduced into a benzene column. Overhead from this column is benzene which is condensed and recycled to the process feed. Bottoms from the benzene column are fed to an ethylbenzene column in which ethylbenzene is separated from the polyethylbenzenes. The overhead stream from this column

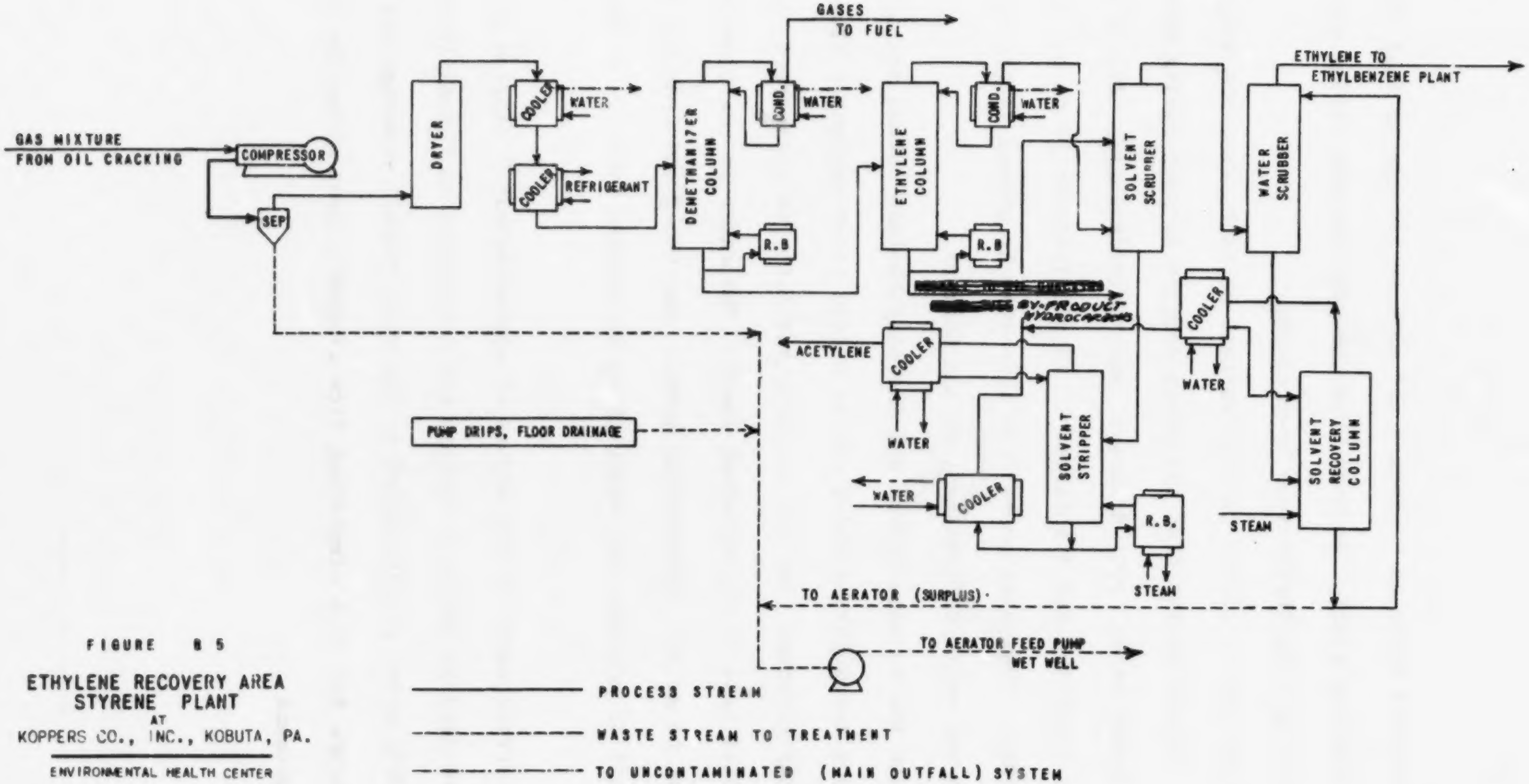
GASES
TO FUEL
ETHYLENE TO
ETHYLBENZENE PLANT
GAS MIXTURE
FROM OIL CRACKING
COMPRESSOR
SEP
DRYER
COOLER
WATER
COOLER
REFRIGERANT
DEMETHANIZER COLUMN
COND.
WATER
R.B
ETHYLENE COLUMN
COND.
WATER
R.B
SOLVENT SCRUBBER
WATER SCRUBBER
BY-PRODUCT HYDROCARBONS
COOLER
WATER
ACETYLENE
COOLER
WATER
PUMP DRIPS, FLOOR DRAINAGE
SOLVENT STRIPPER
WATER
COOLER
R.B.
STEAM
SOLVENT RECOVERY COLUMN
STEAM
TO AERATOR (SURPLUS)
TO AERATOR FEED PUMP
WET WELL
PROCESS STREAM
WASTE STREAM TO TREATMENT
TO UNCONTAMINATED (MAIN OUTFALL) SYSTEM

FIGURE 8 5

ETHYLENE RECOVERY AREA
STYRENE PLANT
AT
KOPPERS CO., INC., KOBUTA, PA.

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is ethylbenzene which is condensed and sent to storage as feed for the styrene cracking plant. Bottoms from the ethylbenzene column are the higher-boiling polyethylbenzene by-products.

There are no liquid process wastes, as such, from the ethylbenzene process. Liquid wastes from the plant consist of pump casing water, compressor jacket water, roof drainage, and floor drainage. All of these flows are collected and discharged to an ethylbenzene plant oil intercepting sump. The water phase from this sump is pumped to the aeration feed pump wet well for treatment in the aerator.

Both the benzene column and the ethylbenzene column are equipped with reflux accumulators which can be vented to an emergency blowdown stack. Any blowdown from the reflux accumulator is discharged into the water-filled base of the blowdown stack. The water in the blowdown stack discharges to an oil intercepting sump. Recovered oil from the sump is returned to process; the water phase discharges directly to Raccoon Creek.

Service water in the amount of approximately 7 million gallons per day is used in indirect coolers and condensers in the ethylbenzene plant. This water is discharged to the main outfall sewerage system.

Figure B-6 is a simplified flow diagram representing the ethylbenzene process.

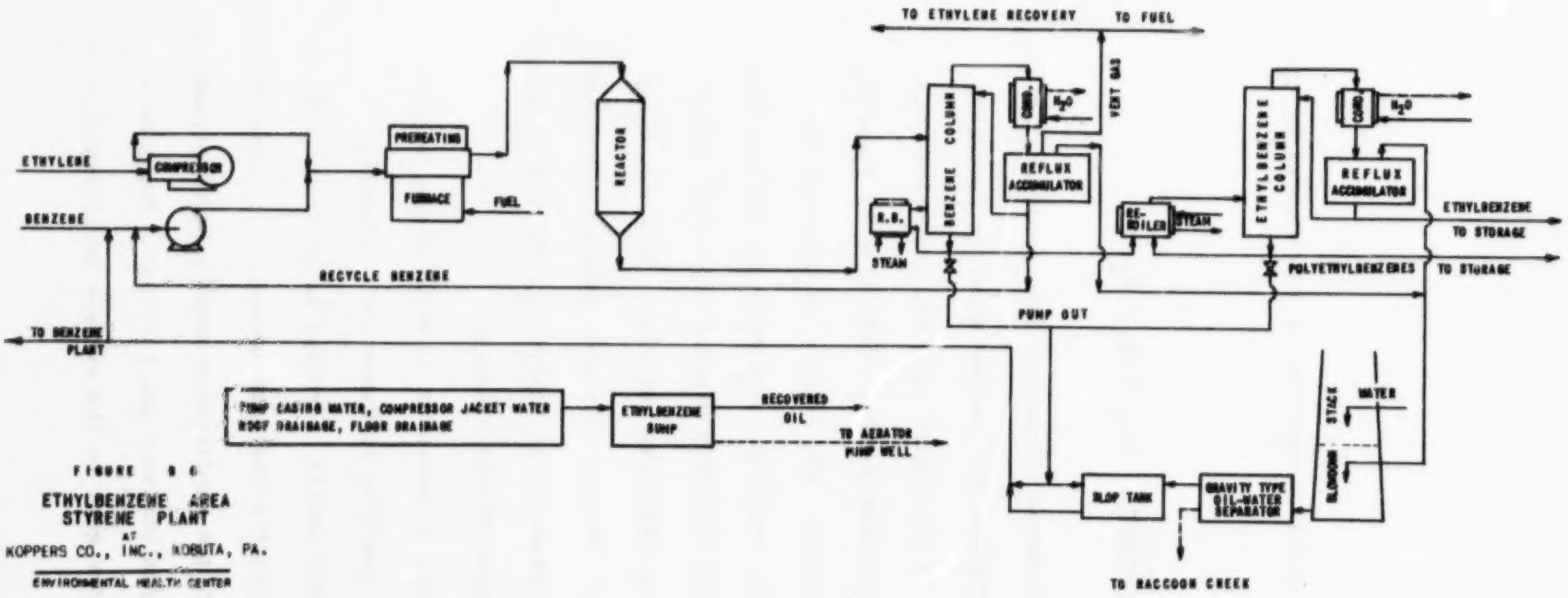
TO ETHYLENE RECOVERY
TO FUEL
VENT GAS
ETHYLENE
COMPRESSOR
BENZENE
PREHEATING
FURNACE
FUEL
REACTOR
R.B.
STEAM
BENZENE COLUMN
COND.
H_2O
REFLUX ACCUMULATOR
RE-BOILER
STEAM
ETHYLBENZENE COLUMN
COND.
H_2O
REFLUX ACCUMULATOR
ETHYLBENZENE
TO STORAGE
POLYETHYLBENZENES
TO STORAGE
RECYCLE BENZENE
PUMP OUT
TO BENZENE PLANT
PUMP CASING WATER, COMPRESSOR JACKET WATER
ROOF DRAINAGE, FLOOR DRAINAGE
ETHYLBENZENE SUMP
RECOVERED OIL
TO AERATOR PUMP WELL
STACK
WATER
BLOWDOWN
SLOP TANK
GRAVITY TYPE OIL-WATER SEPARATOR
TO RACCOON CREEK

FIGURE B 6

ETHYLBENZENE AREA
STYRENE PLANT
AT
KOPPERS CO., INC., KOBUTA, PA.

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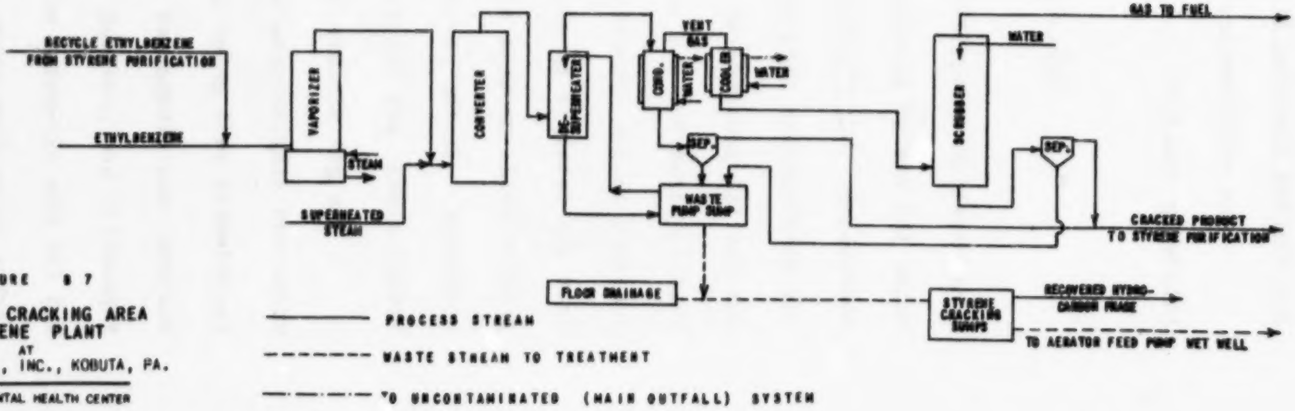
RECYCLE ETHYLBENZENE
FROM STYRENE PURIFICATION
ETHYLBENZENE
VAPORIZER
STEAM
SUPERHEATED STEAM
CONVERTER
DE-SUPERHEATER
VENT GAS
COND.
WATER
COOLER
WATER
SEP.
WASTE PUMP SUMP
SCRUBBER
WATER
GAS TO FUEL
SEP.
CRACKED PRODUCT
TO STYRENE PURIFICATION
FLOOR DRAINAGE
STYRENE CRACKING SUMPS
RECOVERED HYDRO-CARBON PHASE
TO AERATOR FEED PUMP WET WELL
PROCESS STREAM
WASTE STREAM TO TREATMENT
TO UNCONTAMINATED (MAIN OUTFALL) SYSTEM

FIGURE B 7

STYRENE CRACKING AREA
STYRENE PLANT
AT
KOPPERS CO., INC., KOBUTA, PA.

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4. Styrene Cracking Process

The ethylbenzene dehydrogenation reaction is represented by the following equation:

$$C_6H_5.C_2H_5 \xrightarrow[\text{catalyst}]{\text{heat}} C_6H_5.C_2H_3 + H_2$$

Consideration of equilibrium phenomena concerning this reaction indicates the use of elevated temperature and low pressure for favorable conversion. Superheated steam is introduced into the converter with the ethylbenzene feed and accomplishes pressure reduction by lowering the partial pressure of ethylbenzene. The steam also supplies the heat required for the endothermic reaction, maintains the desired temperature in the converter, and continuously removes deposited carbon from the catalyst by means of the water gas reaction. Side reactions produce small amounts of toluene, benzene, methane, ethane, and other compounds. In the process, ethylbenzene is vaporized, mixed with superheated steam, and fed to a catalyst-filled converter.

The gas mixture then enters a condenser in which steam, styrene, unreacted ethylbenzene and side reaction products are condensed. Uncondensed vent gases are further cooled, scrubbed to recover hydrocarbons, and discharged to the plant's fuel gas system. Oil-water separators are provided for both the condensed cracked product stream and for the oil-water mixture from the vent gas scrubber. The hydrocarbon phase from these separators goes to the styrene purification plant for separation and purification of styrene. The water phase goes to the styrene cracking sumps.

Liquid waste from the process is comprised of the water phases from the two separators mentioned above, and floor drainage. The styrene cracking sumps are gravity type separators which discharge their water phase to the aerator feed pump wet well.

Service water use in indirect coolers and condensers in the styrene cracking plant amounts to approximately 17 million gallons per day. This water is discharged to the main outfall sewerage system.

Figure B-7 is a simplified flow diagram representing the styrene cracking process.

5. Styrene Purification Process

The final step in the manufacture of styrene is its separation from unreacted ethylbenzene and the compounds produced by side reactions in the ethylbenzene dehydrogenation process.

The cracked product is fed to a benzene-toluene column, operating under vacuum. Condensable overhead, containing benzene and toluene, is sent to the benzene plant for separation and recovery of materials. Bottoms material goes to the ethylbenzene removal system, which consists of two columns operating under vacuum, in series. Condensable overheads from these columns are returned to the styrene cracking process. Bottoms from the primary ethylbenzene column are cooled and fed to the secondary ethylbenzene column whose bottoms are cooled and sent to storage as crude styrene.

Pure styrene is recovered as condensed overhead from stills operating under vacuum. Bottom residue from the columns is disposed of by burning.

Vacuum is maintained on the columns of the styrene purification system by three-stage steam ejectors with barometric condensers. All non-condensable overheads are discharged to waste with condenser water. The only liquid wastes from this process are overflows from the hot wells of the vacuum system's barometric condensers. At the present time, all hot wells discharge to a common header which in turn discharges to both the sewer system which contributes to the main outfall and the aerator feed pump wet well.

About 13.5 million gallons per day of service water is used in indirect coolers and condensers in the styrene purification plant. This water discharges to the main outfall sewerage system.

Figure B-8 is a simplified flow diagram representing the styrene purification process.

6. Miscellaneous Processes

In addition to the processes for the production of styrene which have been described, two other processes are in use at the Kobuta plant. One is the production of divinylbenzene. This process will not be discussed in detail. Its wastes are combined with, and treated with styrene plant wastes.

The second process not involved in the production of styrene is the polymerization of styrene to polystyrene. Details of this process are not available for discussion. One waste stream from the polystyrene unit is neutralized and discharged to Racoon Creek; another discharges to the storm sewer system.

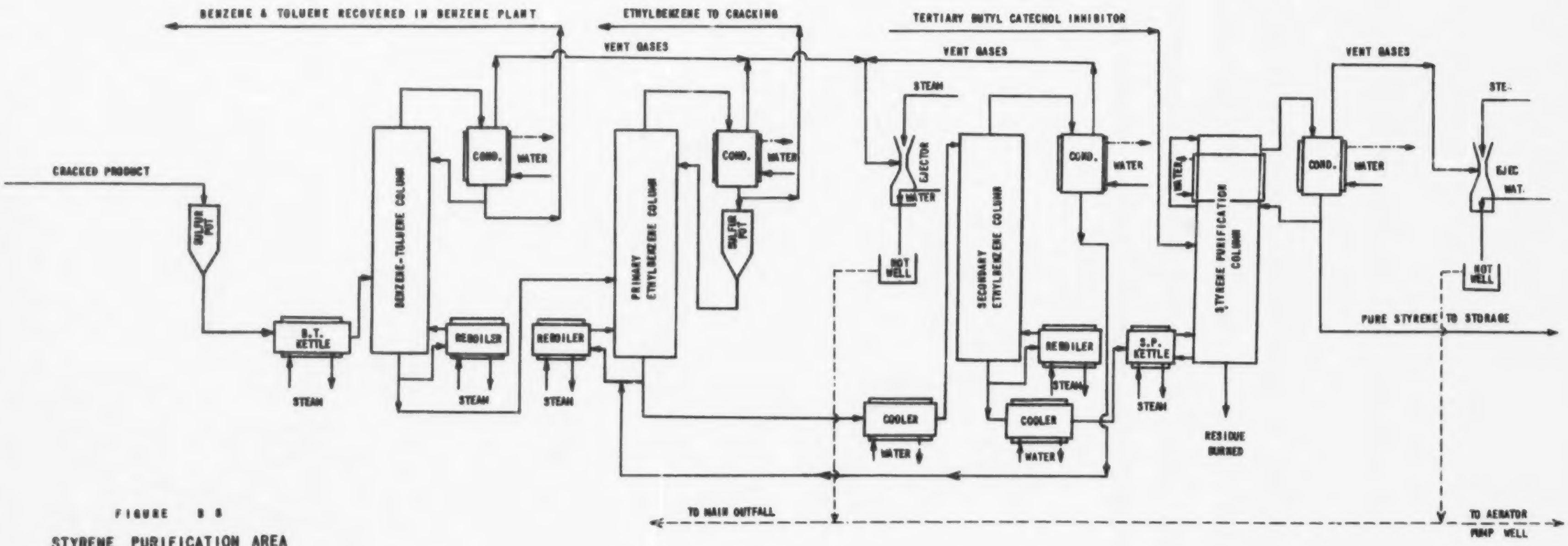

BENZENE & TOLUENE RECOVERED IN BENZENE PLANT
ETHYLBENZENE TO CRACKING
TERTIARY BUTYL CATECHOL INHIBITOR
VENT GASES
VENT GASES
VENT GASES
CRACKED PRODUCT
SULFUR POT
B.T. KETTLE
STEAM
BENZENE-TOLUENE COLUMN
COND.
WATER
REBOILER
STEAM
REBOILER
STEAM
PRIMARY ETHYLBENZENE COLUMN
COND.
WATER
SULFUR POT
STEAM
EJECTOR
WATER
HOT WELL
COOLER
WATER
SECONDARY ETHYLBENZENE COLUMN
COND.
WATER
REBOILER
STEAM
COOLER
WATER
S.P. KETTLE
STEAM
WATER
STYRENE PURIFICATION COLUMN
RESIDUE BURNED
COND.
WATER
STE-
EJEC
WAT.
HOT WELL
PURE STYRENE TO STORAGE
TO MAIN OUTFALL
TO AERATOR PUMP WELL
PROCESS STREAM
WASTE STREAM TO TREATMENT
TO UNCONTAMINATED (MAIN OUTFALL) SYSTEM

FIGURE B 8

STYRENE PURIFICATION AREA
STYRENE PLANT
AT
KOPPERS CO., INC., KOBUTA, PA.

ENVIRONMENTAL HEALTH CENTER

STYRENE PLANT PROCESS WASTES SUMMARIZED

A brief summary and discussion of the process wastes from the styrene plant is presented for convenient reference.

7. Benzene Plant

Waste sources in the benzene plant are the four water separators, through which the condensed overhead streams from the distillation columns pass, and agitator wash water. Water from these separators has been in direct contact with process materials. It is expected that in each case the water will be saturated with the contacted material and contain as well some of the hydrocarbon in emulsion. Room temperature solubilities, in pounds per gallon of water, for known process materials in contact with the waste waters, are as follows:

Benzene	0.0068
Ethylbenzene	.0012
Toluene	.0039

The xylenes are considered essentially insoluble. Wastes from this process pass through an oil-intercepting sump and discharge to the aerator feed pump wet well.

8. Ether-Ethylene Plant

The process waste source in the ether-ethylene plant is the ethylene gas water scrubbing tower. Water discharged from this scrubber includes both that produced in the dehydration of ether to ethylene and that introduced to accomplish scrubbing of the ethylene gas. Water produced in the reaction probably accounts for not more than one or two per cent of the flow from the tower. The solubility of ethylene at a partial pressure of one atmosphere in cold water is about 0.0[illegible]7 pound per gallon; that of liquid ether is about 0.6 pound per gallon of water at 20°C. While water from the scrubbing tower may approach saturation with ethylene, it is not expected that such is the case with ethyl ether. Water from the tower will also contain small amounts of acids and aldehydes. Process waste and floor drainage from this plant are pumped to the aerator feed pump wet well.

9. Oil Cracking Plant

Wastes from the oil cracking process consist of the water phase from two oil-water separators. These include process wastes and miscellaneous minor wastes such as floor drainage, compressor knockout, etc. The wastes may be expected to contain crude oil as well as various constituents resulting from the thermal cracking of crude oil. Spent caustic from the cracked product sweetening operation is also included in these wastes. Other materials which have been shown to be present in petroleum refinery wastes, all or some of which may also be present in wastes from this process, are phenols, mercaptans, nitrogen bases, naphthenic acids, and various inorganic compounds which may have been present as impurities in the crude oil. Wastes from this process are pumped to the butadiene waste oil skimmer.

10. Ethylene Recovery Plant

Process wastes from the ethylene recovery plant include scrubbing water from the ethylene gas scrubbing column, compressor knockout from the cracked gas stream from the oil cracking plant (process feedstock), and pump drips and floor drainage from the process area. Water from the ethylene gas water scrubber may be expected to contain ethylene (solubility 0.0027 lb/gal of cold water at one atmosphere pressure), any of the acetylene removal solvent carried over in the ethylene stream from the preceding solvent scrubbing tower, and any other water-soluble materials which have been carried in the ethylene stream through the process. This water is steam-stripped in the solvent recovery still whose bottoms are discharged to the aerator. Compressor knockout, pump drips, and floor drainage, are contaminated with the various constituents of the cracked gas mixture which is fed to the process. All process wastes, pump drips, and floor drainage are pumped to the aerator feed pump wet well. The ethylene recovery plant is not equipped with a separator sump.

11. Ethylbenzene Plant

Wastes from the ethylbenzene plant consist of compressor jacket water, pump casing water, floor drainage, and roof drainage. These wastes pass through an oil intercepting sump and are pumped to the aerator feed pump wet well. Contamination of these waste streams apparently results from leaks and spills. Solubilities of benzene and ethylene are listed above. The solubility of ethylbenzene at room temperature is about 0.001 pound per gallon of water. Polyethylbenzenes are reportedly insoluble in water.

12. Styrene Cracking Plant

Ethylbenzene is catalytically cracked to styrene in the presence of superheated steam. Following the cracking operation, the reaction mixture is condensed and separated, the condensed steam going to waste. Vent gases from the cracking operation are water-scrubbed. The scrubbing water from this operation passes through a separator, the water phase from which goes to waste. Wastes from both of these sources, along with floor drainage, are pumped to the styrene sumps which are gravity type oil water separators. The water phase from these sumps is discharged to the aerator feed pump wet well. The solubility of ethylbenzene, as previously mentioned, is about 0.001 pound per gallon of water at room temperature. Styrene is reported as being very slightly soluble in water; no definite solubility figure being available. Wastes from this plant will contain ethylbenzene and styrene in solution, and probably in emulsion as well, along with organic materials scrubbed from the vent gas stream.

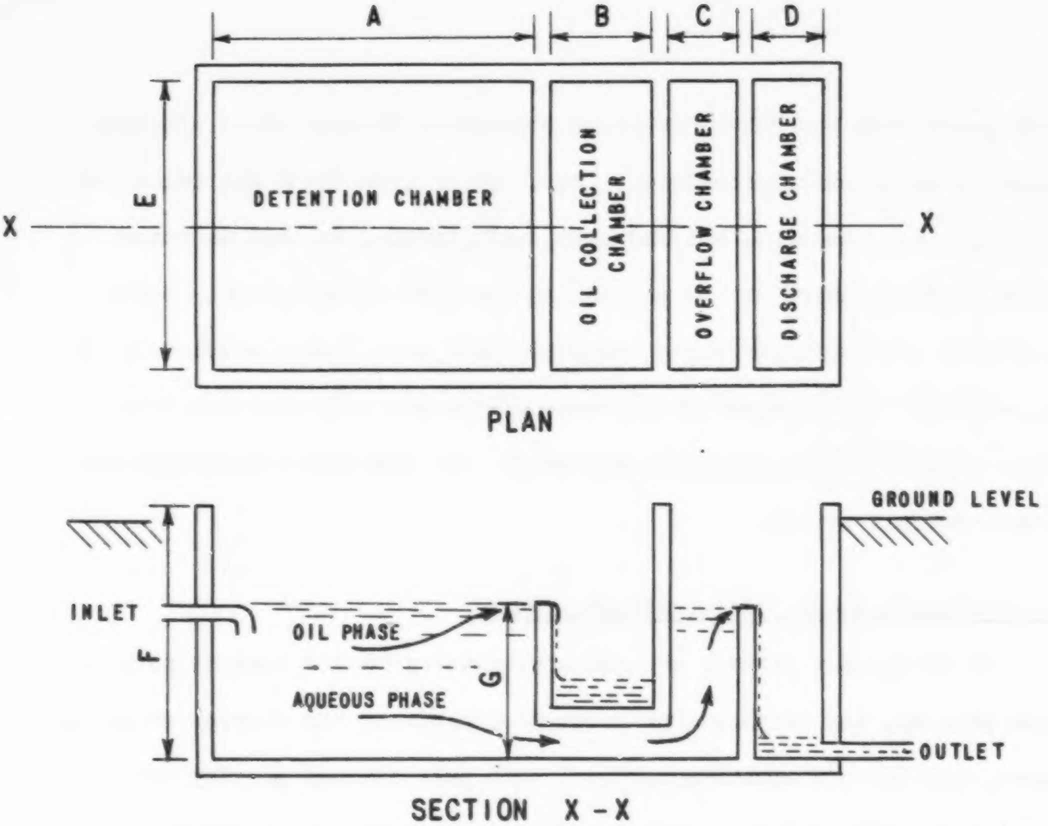
13. Styrene Purification Plant

Process waste from the styrene purification plant consists of the overflow from the barometric condenser hot wells. Vacuum is maintained on the various columns used in the purification process by passing uncondensed gases from the column overhead condensers through steam ejectors equipped with barometric condenser legs. Water from these hot wells can contain benzene, toluene, ethylbenzene, and styrene, as well as other lighter organics which may be present in the feed to the plant. Solubility data available for these compounds have been listed previously in this section. An estimated 60 per cent of the hot well overflow discharges to the aerator feed pump wet well; the remainder discharges to the main outfall system.

14. Individual Plant Oil Intercepting Sumps

As previously stated, the process wastes from the benzene purification process, the ethylbenzene production process, the styrene cracking process, and the oil cracking process, each pass through gravity type oil-water separators before entering the plant's main waste treatment facilities. The design and dimensions of these intercepting sumps are shown in Figure B-9. The benzene sump consists of two units placed side by side. These units may be operated alternately or in parallel. The ethylbenzene sump and oil cracking sump each consist of one unit only. The styrene cracking sump consists of seven units operated in parallel. Five of these seven units receive wastes from the styrene cracking operation, two receive wastes from the divinyl benzene operation; all seven overflow to a common discharge chamber.

In addition to the conventionally disigned oil cracking sump which receives miscellaneous wastes, the oil cracking plant has in the process a product separator which discharges an aqueous phase to the process waste


A
B
C
D
E
X
X
DETENTION CHAMBER
OIL COLLECTION CHAMBER
OVERFLOW CHAMBER
DISCHARGE CHAMBER
PLAN
GROUND LEVEL
INLET
OIL PHASE
AQUEOUS PHASE
F
G
OUTLET
SECTION X - X

SEPARATING SUMP	THEORETICAL DETENTION TIME - HRS.	NUMBER OF PARALLEL UNITS	APPROXIMATE DIMENSIONS - FEET						
			A	B	C	D	E	F	G
BENZENE SUMP	2.6	2	15	4.5	3	3	5	10.7	4.5
ETHYLBENZENE SUMP	0.3	1	8	4	2	3	6.8	10	5.6
STYRENE CRACKING SUMP	1.8	7	25.5	4.3	3	3	6	11.8	6.6
OIL CRACKING SUMP		1	14	*	1	1	6	8.2	2.2

* FLOATING OIL COLLECTED BY MEANS OF HORIZONTAL SLOTTED PIPE ACROSS DOWNSTREAM END OF DETENTION CHAMBER.

FIGURE B 9

INDIVIDUAL PLANT PROCESS WASTE
OIL INTERCEPTING SUMP DESIGN
AT
KOPPERS CO., INC., KOBUTA, PA.

ENVIRONMENTAL HEALTH CENTER

system. This separator, known as the "V-5" separator, is a 20,000 gallon cylindrical tank which receives the condensed cracked product from the oil cracking reactor. This tank is equipped with an automatic device which controls the level of the oil-water interface. The combined wastes from the oil cracking sump and the V-5 separator are pumped to the butadiene waste oil skimmer.

All of the intercepting sumps are equipped with stand-by pumps.

In no case were samples of process wastes taken ahead of any of the individual plant process waste oil intercepting sumps described above. From these plants, the so-called untreated waste streams sampled are those between the individual plant separators and the main plant waste treatment facilities, the aerator and the butadiene waste oil skimmer.

SURVEY PROCEDURES

15. Sample Collection

The sampling program for the investigation of Kobuta plant wastes involved the collection of samples four days per week during the period May 14 through June 19, 1952. The collection of samples in the plant was accomplished by Koppers Company personnel. All samples within the styrene plant were composites of increments taken at hourly intervals for periods either of 8 hours or 24 hours. It will be noted that at the majority of sampling locations discussed in this part of the report, samples were taken for a period of two days only. The reason for this sharp limitation of the number of samples is discussed at the end of the section entitled "General Information."

The following tabulation (Table B-2) shows the number of hours represented by the composite samples and the number of days samples were taken at each sampling point within the styrene plant. (See Figure C-1 and Figure C-2 for location of sampling points).

Samples of Group I of this table represent process wastes from styrene operations. Samples at these points are intended to show the nature of various individual process wastes, and combinations of wastes, which make up the flow to the waste treatment facilities. Process wastes are those which originate in the process, or those which have been in direct contact with contaminating materials in the process.

Group II is a list of sampling locations in the uncontaminated waste system. Flows in this system are essentially water which has been used only as a cooling medium in indirect coolers and condensers. These streams should be uncontaminated except for leaks or accidental losses, or for contaminated roof or yard drainage entering at storm grates. Two exceptions to this general statement can be found in the styrene area: one, a portion of the styrene purification hot well overflow is discharged to the storm system, and two, a portion of the process wastes from polystyrene operations enters this system.

Group Number III is self-explanatory.

16. Flow Measurements

The means of obtaining flow data for each of the sampling points described in this part of the report are shown below.

Table B-2 - Styrene Plant Sampling Points

	Sampling Point	Hours Composited	Days Sampled
I. **Sampling Point Locations Involving Styrene Plant Process Wastes Prior to Treatment** (Contaminated Wastes)			
a. Aerator influent	8	24 8	8 4
b. Oil cracking plant wastes to butadiene oil skimmer	5-b	8	4
c. Styrene purification hot wells overflow to aerator	S-4	8	2
d. Benzene, ethylene, ethylene recovery and ethylbenzene wastes to aerator	11	8	2
e. Styrene cracking sump waste to aerator	12	8	2
f. Ethylbenzene sump discharge	14	8	2
g. Benzene sump discharge	15	8	2
h. Ethylene pump discharge	16	8	2
II. **Sampling Point Locations for Styrene Plant Contributions to the Storm Sewers (Main Outfall) System** (Uncontaminated Wastes)			
a. Benzene plant area	42	8	2
b. Ethylene plant area	36	8	4
c. Acetylene removal, ethylene plant, ethylene recovery, and ethylbenzene areas	33	8	4
d. Acetylene removal area	I	8	2
e. Styrene cracking plant area	Q	8	2
f. Styrene cracking plant area	37	8	2
g. Styrene purification plant area	R	8	2
h. Styrene purification and benzene plant areas	38	8	2
III. **Styrene Plant Wastes to Raccoon Creek**			
a. Oil cracking plant cooling and condenser water plus neutralized polystyrene wastes	V	8	2

I. Contaminated System

Aerator Influent - The aerator influent line is equipped with an orifice plate and recorder. Flow to the aerator was determined from the recorder chart.

Oil Cracking Plant Process Waste - The flow value used is the average daily value for the month of May, taken from the plant's utilities records.

Styrene Purification Hot Wells - Information furnished by Koppers Company indicates an average flow of 525 gallons per minute through the barometric condensers to the hot wells. The hot wells overflow to a common header which discharges both to the aerator feed pump wet well and to the uncontaminated (main outfall) system. It was estimated that 60 per cent of the flow from the hot wells goes to treatment and that the remaining 40 per cent goes to the main outfall system.

Benzene, Ethylene, Ethylene Recovery, and Ethylbenzene Wastes to Aerator - The volume of this flow was determined by deducting the volumes of the styrene purification hot well waste and the styrene cracking waste from the measured volume of aerator influent.

Styrene Cracking Sump Waste to Aerator - The flow value used is the average daily value for the month of May, taken from the plant's utilities records.

Ethylbenzene Sump Discharge - This waste is pumped by a piston type pump to the aerator feed pump wet well. The quantity of this waste was determined by observing, at the time each sample increment was taken, the number of strokes per unit time of the positive displacement pump and calculating with displacement values the volume of the waste.

Benzene Sump Discharge - This waste is pumped by a piston type pump. Its volume was obtained in the same manner as that from the ethylbenzene sump.

Ethylene Pump Discharge - This waste, too, is pumped by a piston type pump. Its volume was obtained in the same manner as that from the ethylbenzene and benzene sumps.

II. Uncontaminated System

Benzene Plant Area - The volume of this waste was determined for the days sampled from the plant's utilities records.

The flow values used for all of the remaining eight sampling points listed in Groups II and III of Table B-2 are the average daily values for the month of May, taken from the plant's utilities records.

The plant's utilities records were based upon metered (orifice plate) water usage records.

17. Laboratory Analyses

The following routine determinations were made on the majority of samples collected:

Threshold odor (hot and cold)
Oxygen consumed, by $K_2Cr_2O_7$
5-day biochemical oxygen demand
pH

In addition to these routine determinations, phenols and oil were determined for selected samples from various sampling points. Threshold odor values were also expressed as pO values according to the 8th Edition of "Standard Methods for the Examination of Water and Sewage." (1) Fractional, rather than whole, numbers were used to point out small differences. The procedures used in making the above analyses were, in general, those outlined in "Standard Methods for the Examination of Water and Sewage," 9th Edition. (2) The dilution technique for threshold odor was not followed. Successive dilution ratios, with odor-free water, of 2:1 were used in order to conform to the physiological Weber-Fechner law, that is, each successive dilution was one-half that of the previous one.

Modified methods used for the determination of oxygen consumed by $K_2Cr_2O_7$, phenols, and oils, are discussed in the final appendix of this report.

18. Explanation of Laboratory Analyses

A brief explanation of the various laboratory determinations is given in the appendix at the end of this report, and is intended to serve as an aid in the interpretation of the analytical results reported.

DISCUSSION OF RESULTS

The Kobuta styrene plant operates on a continuous basis, 24 hours per day, with an estimated normal daily production of 140 tons of styrene. Operation of the plant, or various portions of the plant, may at times be curtailed or accelerated, depending upon economic considerations or the availability of raw materials. Fluctuations in the quantity and quality of wastes produced by the various plants may be caused by maintenance or operational difficulties or by changes in production levels.

Analyses were made of the raw service water being pumped into the plant from the Ohio River. This was done in order that the concentration of the various constituents found in the river water might be deducted from the concentrations of these constituents found in plant wastes to obtain a net value for the quantity of each contaminant chargeable to plant operation.

Appendix Table B-1 is a tabulation of the gross concentrations and quantities of constituents of the waste streams from the styrene plant as represented by the individual samples collected during the period of the survey. Table B-3 is a tabulation of the average gross concentrations and quantities of constituents of each waste stream, the average concentrations and quantities of these constituents chargeable to the river water influent to the plant, and the net concentrations and quantities of the constituents chargeable to the plant operations.

Chemical Division
Koppers Company
Kobuta, Penna.

Table B-3 - Gross and Net Values for Average Concentrations and Quantities of Waste Constituents at Styrene Plant

	Flow MGD	Threshold Odor Number		pO		Weighted Threshold Odor		Oxygen Consumed, by $K_2Cr_2O_7$		5-Day B.O.D.	
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day
Benzene Purification Plant Waste Sump Effluent, Sampling Point No. 15											
Gross	0.046	1,100	1,550	10.1	10.6	51	71	1,340	510	1,000	390
River water		36	72			2	3	24	10	2	1
Net		1,060	1,480	10.0	10.5	49	68	1,320	500	1,000	390
Ether-Ethylene Plant Wastes Pumps Discharge, Sampling Point No. 16											
Gross	0.044	1,100	1,550	10.1	10.6	48	68	1,430	470	1,020	330
River water		36	72			1	3	24	9	2	1
Net		1,060	1,480	10.1	10.5	47	65	1,410	460	1,020	330
Ethylbenzene Plant Waste Sump Effluent, Sampling Point No. 14											
Gross	0.194	1,100	780	10.1	9.6	213	151	> 590	> 960	430	700
River water		36	72			7	14	24	40	2	3
Net		1,060	710	10.0	9.4	206	137	> 570	> 920	430	700
Combined Benzene, Ethylene, Ethylene Recovery, & Ethylbenzene Process Wastes, Samplint Point No.11											
Gross	0.60	550	2,200	9.1	11.1	330	1,320	610	3,040	> 270	> 1,360
River water		6	12			4	7	24	120	2	10
Net		540	2,190	9.1	11.1	326	1,310	590	2,920	> 270	>1,350
Styrene Cracking Plant Waste Sump Effluent, Sampling Point No. 12											
Gross	0.71	280	1,100	8.1	10.1	200	780	300	1,750	> 370	> 2,200
River water		6	12			4	8	24	140	2	12
Net		274	1,090	8.1	10.1	194	772	276	1,610	> 370	> 2,190
Styrene Purification Plant Hot Wells Effluent, Sampling Point No. S-4											
Gross	0.45	390	390	8.6	8.6	180	180	92	350	32	120
River water		6	12			3	6	24	90	2	8
Net		384	380	8.6	8.6	177	174	68	260	30	112
Aerator Influent, Sampling Point No. 8											
Gross	1.46	6,250	3,600	12.6	11.8	9,130	5,260	564	6,730	316	3,760
River water		13	12			19	18	24	290	2	24
Net		6,240	3,590	12.6	11.8	9,110	5,240	540	6,440	314	3,740
Oil Cracking Waste to Butadiene Waste Oil Skimmer, Sampling Point No. 5-b											
Gross	0.216	49,200	86,000	15.6	16.4	10,600	18,600	15,900	28,600	9,300	16,700
River water		7	24			2	5	24	40	2	4
Net		49,200	86,000	15.6	16.4	10,600	18,600	15,900	28,600	9,300	16,700
Benzene Plant Area, Sampling Point No. 42											
Gross	0.82	49	74	5.6	6.2	40	61	48	220	30	130
River water		24	20			20	16	3	20	1	5
Net		25	54	4.3	5.0	20	45	45	200	29	125

Chemical Division
Koppers Company
Kobuta, Penna.

Table B-3 (Continued) - Gross and Net Values for Average Concentrations and Quantities of Waste Constituents at Styrene Plant

	Flow MGD	Threshold Odor Number		pO		Weighted Threshold Odor		Oxygen Consumed, by $K_2Cr_2O_7$		5-Day B.O.D.	
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day
Benzene-Styrene Purification Plant Areas, Sampling Point No. 38											
Gross	2.31	23	23	4.5	4.5	53	53	19	360	3.0	58
River Water		6	12			14	28	13	250	3.6	69
Net		17	11	3.9	2.3	39	25	6	110	-	-
Acetylene Removal Unit Yard Level Sump Discharge, Sampling Point No. I											
Gross	1.09	4	4	2	2	4.4	4.4	4	37	1.3	11.5
River Water		2	9			2.2	9.8	13	122	0.8	7.6
Net		2	0	1	1.3	2.2	0	0	0	0.5	3.9
Ethylene Plant Area, Sampling Point No. 36											
Gross	2.07	830	1,020	9.7	10.0	1,720	2,110	57	980	60	1,040
River Water		25	40			50	80	13	224	1	20
Net		805	980	9.6	9.9	1,670	2,030	44	756	59	1,020
Acetylene Removal, Ethylene Plant, Ethylene Recovery & Ethylbenzene Plant Areas, Sampling Point No. 33											
Gross	10.5	210	180	7.7	7.5	2,210	1,890	61	5,360	23	2,010
River Water		25	40			260	420	13	1,140	1	80
Net		185	140	7.6	5.8	1,950	1,470	48	4,220	22	1,930
Styrene Purification Area, Sampling Point No. R											
Gross	13.4	64	90	6.0	6.5	860	1,210	19	2,140	7.2	800
River Water		24	20			320	270	3	320	0.8	85
Net		40	70	3.4	4.0	540	940	16	1,820	6.4	715
Styrene Cracking Area, Sampling Point No. Q											
Gross	11.4	10	7	3.3	2.8	110	80	7.0	670	1.9	180
River Water		24	20			270	230	2.9	275	0.8	72
Net		0	0	0	0	0	0	4.1	395	1.1	108
Styrene Cracking Area, Sampling Point No. 37											
Gross	5.7	12	12	3.6	3.6	68	68	11	510	1.3	61
River Water		24	20			136	114	3	135	0.8	36
Net		0	0	2.0	2.3	0	0	8	275	0.5	25
Oil Cracking and Polystyrene Wastes to Raccoon Creek, Sampling Point No. V											
Gross	8.40	20	14	4.3	3.[illegible]	170	120	8	570	4.5	320
River Water		2	9			17	76	13	910	0.8	56
Net		18	5	4.2	1.7	153	44	0	0	3.7	264

19. Contaminated (Concentrated) Waste System

Of the seven distinct processes employed in the styrene plant, the process waste streams from six were sampled individually. These streams were the wastes from the benzene purification process, the ether-ethylene process, the oil cracking process, the ethylbenzene process, the styrene cracking process, and the styrene purification process. Wastes from the seventh process, ethylene recovery, were not sampled individually but were included in combination with other wastes at two sampling points prior to treatment.

The following tabulation of processes, with net values for various constituents of the process waste streams sampled, indicates the relative contribution of each:

Table B-4 - Styrene Plant Process Wastes; Quantities of Waste Constituents

Process	Sampling Point	Flow MGD	Weighted Threshold Odor (Cold)	Oxygen Consumed lb/day	B.O.D. lb/day
Wastes to aerator:					
Benzene purification*	(15)	0.046	49	500	390
Ether ethylene*	(16)	0.044	47	460	330
Ethylbenzene*	(14)	0.194	210	920	700
Ethylene recovery	Not sampled				
Combined benzene, ethylene, ethylbenzene, and ethylene recovery	(11)	0.60	330	2,920	>1,350
Styrene cracking	(12)	0.71	190	1,610	2,190
Styrene purification	(S4)	0.45	180	260	112
Total		1.76	700	4,790	>3,650
Aerator influent	(8)	1.46	9,110	6,440	3,740
Waste to butadiene waste oil skimmer:					
Oil cracking	(56)	0.216	10,600	28,600	16,700
Total styrene process wastes		1.68	19,700	35,040	20,440

* These wastes are not included in the total since they are included in the flow at sampling point 11.

The very poor agreement between the sum of the weighted threshold odor values of the wastes which combine to make the aerator influent and the weighted threshold odor value for the aerator influent will be noted. The individual wastes were sampled during the latter part of the study only. Several very high weighted threshold odor values for the aerator influent were obtained early in the study. These high values are largely responsible for the wide discrepancy.

Comparison of these data for the oil cracking waste with the corresponding data for the aerator influent, which includes all other process wastes from styrene operations, shows that more than 80 per cent of the oxygen demand of the styrene plant untreated process wastes is due to the oil cracking plant. The oil cracking plant waste accounts for more than 40 per cent of the process waste weighted threshold odor from styrene operations.

The styrene cracking process waste, represented by sampling point number 12, exhibits the greatest combined threshold odor, oxygen consumed, and B.O.D. effect of the six process wastes tributary to the aerator. The ethylbenzene process waste, represented by sampling point number 14, makes the second-greatest contribution of the total quantities of these constituents to the aerator influent. The process wastes from the benzene purification plant, the ether-ethylene plant, the ethylene recovery plant, and the styrene purification plant, all contribute roughly the same quantities of these combined waste constituents to the treatment facilities.

The benzene purification and ether-ethylene wastes exhibit the highest concentrations of constituents of the six wastes tributary to the aerator. Their total quantitative contribution of waste constituents is relatively low because of their very low volumes. The ethylbenzene plant waste exhibits the next highest concentrations, and even though the waste has less than average volume, these concentrations of waste constituents make the ethylbenzene plant the second-greatest contributor of total quantity of waste constituents to the aerator. The styrene cracking plant discharges such a large volume of relatively dilute waste that it contributes the greatest quantity of combined waste constituents to the aerator. The wastes from the ethylene recovery and styrene purification plants are quite dilute, and even with a combined flow representing some 50 per cent of that to the aerator, these two wastes contribute together only about 20 per cent of the total quantity of waste constituents.

20. Uncontaminated (Dilute) Waste System; Not Treated

Flows at eight of the sampling points in the untreated, or main outfall, sewerage system, originate in the styrene process area. The following tabulation of net average values, for various constituents of the waste streams sampled, indicates the contribution of each flow.

Table B-5 - Styrene Plant Dilute Wastes to Main Outfall
Net Quantities of Waste Constituents

Contributing Area	Sampling Point	Flow MGD	Weighted Threshold Odor (Cold)	Oxygen Consumed lb/day	B.O.D. lb/day
Benzene plant area (1)	42	0.82	20	200	125
Benzene, styrene purification plant areas	38	2.31	39	110	-(3)
Acetylene removal plant (1)	I	1.09	-(3)	-(3)	-(3)
Ethylene plant area (1)	36	2.07	1670	756	1,020
Acetylene removal, ethylene plant, ethylene recovery, and ethylbenzene plant areas	33	10.52	1950	4,220	1,930
Styrene purification area	R	13.4	540	1,820	715
Styrene cracking area	Q	11.4	-(3)	395	108
Styrene cracking area	37	5.7	-(3)	373	25
Total (2)		43.3	2530	7,020	2,780

(1) These sampling points are not included in the total, since their flows are included in the flows at other listed sampling points.

(2) Total does not include the small amount of waste constituents discharged directly to Raccoon Creek (Sampling Point No. V).

(3) Negligible quantities; not significant.

The flow at sampling point 42 is included in the flow at sampling point 38, and the flows at sampling points I and 36 are included in the flow at sampling point 33.

The flow from the ethylene plant area, as represented by data for sampling point 36, is the strongest of the sampled wastes discharged untreated from the styrene production area through the main outfall sewerage system.

The strength of this waste is approximately one-eighth that of the styrene plant process wastes entering the aerator for treatment. The total quantities of waste constituents, on a pounds-per-day basis, for the sampled main outfall flows from the styrene production area, are approximately the same as the quantities of the same constituents in the styrene production process wastes being sent to the aerator. The approximate strengths of these two waste flows are therefore in inverse ratio to their volumes, the combined process wastes tributary to the aerator having about thirty times the concentration of contaminants indicated for the styrene production area wastes tributary to the main outfall.

One waste flow from the oil cracking and polystyrene operations is discharged untreated directly to Raccoon Creek. This waste consists of cooling and condenser water from the oil cracking plant and some process waste from the polystyrene plant. This waste, identified as Oil Cracking and Polystyrene Wastes to Raccoon Creek, Sampling Point No. V, exhibits the following characteristics as shown in Table B-3: flow, 8.4 MGD; weighted threshold odor (cold), 153; oxygen consumed by $K_2Cr_2O_7$, nil; 5-day BOD, 264 pounds per day. These values show that, at the time of sampling, this waste was much more dilute than the combined styrene plant dilute wastes discharged to the main outfall sewerage system.

21. Total Wastes from Styrene Plant

The following tabulation, Table B-6, lists the total waste flows and quantities of waste constituents resulting from styrene production operations. It will be noted that the values shown for the process wastes are the quantities of constituents found in these wastes prior to treatment. Waste treatment is discussed in a later part of this report.

Table B-6 - Total Net Quantities of Waste Constituents Discharged Daily from Styrene Area

	Flow MGD	Weighted Threshold Odor (Cold)	Oxygen Consumed lb/day	BOD lb/day
Concentrated wastes (treated subsequently)	1.68	19,700	35,040	20,440
Dilute wastes to main outfall (untreated)	43.3	2,530	7,020	2,780
Wastes to Raccoon Creek (untreated)	8.4	150	0	260
Total	53.4	22,380	42,000	23,500

Unit values for the volume of waste and the quantities of waste constituents found in both the raw process wastes and the styrene production area dilute wastes, per ton of styrene produced, are shown in Table B-7.

Table B-7 - Raw Waste Unit Values per Ton of Styrene Produced

	Volume gallons	Weighted Threshold Odor Units (Cold)	Oxygen Consumed pounds	B.O.D. pounds
Concentrated wastes; subsequently treated:				
Benzene purification	300	0.35	3.57	2.78
Ether-ethylene	300	0.34	3.29	2.35
Ethylbenzene	1,400	1.50	6.57	4.98
Combined benzene, ethylene, ethylbenzene and ethylene recovery	4,300	2.36	20.8	9.64
Styrene cracking	5,100	1.36	11.5	15.6
Styrene purification	3,200	1.29	1.86	0.80
Aerator influent	10,420	65	46	26.7
Oil cracking (1)	1,540	76	204	119
Total	12,000	141	250	146
Total styrene production area dilute wastes to main outfall	309,000	18.1	50	19.8
Total styrene production area dilute wastes direct to Raccoon Creek	59,000	1.1	0	1.9
GRAND TOTAL	380,000	160	300	168

(1) Treated with butadiene concentrated wastes in oil skimmer and stills.

Chemical Division
Koppers Company
Kobuta, Pennsylvania

TABLE B-1 - SUMMARY OF DAILY ANALYSES

STYRENE OPERATIONS - CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS, DAILY VALUES

Date 1952	Flow MGD	Threshold Odor Number Cold (1)	Threshold Odor Number Hot(1)	pO Cold	pO Hot	Weighted Odor (Threshold) Cold(2)	Weighted Odor (Threshold) Hot(2)	O_2 Consumed $K_2Cr_2O_7$ ppm	O_2 Consumed $K_2Cr_2O_7$ lb/day	5-Day B.O.D. ppm	5-Day B.O.D. lb/day	pH
BENZENE PURIFICATION PLANT WASTE SUMP EFFLUENT, SAMPLING POINT NO.15 8 hour composite (increment each hour)												
June 18	0.037	800	800	9.6	9.6	29.6	29.6	1400	431	940	290	6.8
June 19	0.056	1600	3200	10.6	11.6	89.6	179.2	1280	597	1070	499	3.7
Average	0.046	1100	1550	10.1	10.6	51	71	1340	510	1000	390	
ETHER-ETHYLENE PLANT WASTES PUMP DISCHARGE, SAMPLING POINT NO.16 8 hour composite (increment each hour)												
June 18	0.037	1600	1600	10.6	10.6	59.2	59.2	2380	734	1760	542	4.9
June 19	0.052	800	1600	9.6	10.6	41.6	83.2	482	209	274	119	5.5
Average	0.044	1100	1550	10.1	10.6	48	68	1430	470	1020	330	
ETHYLBENZENE PLANT WASTE SUMP EFFLUENT, SAMPLING POINT NO.14 8 hour composite (increment each hour)												
June 18	0.198	800	400	9.6	8.6	158	79	804	1326	541	892	6.6
June 19	0.189	1600	1600	10.6	10.6	302	302	>380	>598	318	500	7.1
Average	0.194	1100	780	10.1	9.6	210	150	>590	>960	430	700	
COMBINED BENZENE, ETHYLENE, ETHYLENE RECOVERY, AND TEHYLBENZENE PROCESS WASTES, SAMPLING POINT NO.11 8 hour composite (increment each hour)												
June 16	0.63	800	1600	9.6	10.6	504	1008	492	2580	>250	>1312	5.2
June 17	0.58	400	3200	8.6	11.6	232	1856	725	3500	>290	>1400	3.4
Average	0.60	550	2200	9.1	11.1	330	1320	610	3040	>270	>1360	

(1) Average threshold odor values are geometric means.

(2) Average weighted threshold odor values are products of average threshold odors and flows in millions of gallons per day.

TABLE B-1 - SUMMARY OF DAILY ANALYSES

STYRENE OPERATIONS - CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS, DAILY VALUES Cont'd-2

Chemical Division
Koppers Company
Kobuta, Pennsylvania

Date 1952	Flow MGD	Threshold Odor Number Cold	Threshold Odor Number Hot	pO Cold	pO Hot	Weighted Odor (Threshold) Cold	Weighted Odor (Threshold) Hot	O_2 Consumed $K_2Cr_2O_7$ ppm	O_2 Consumed $K_2Cr_2O_7$ lb/day	5-Day B.O.D. ppm	5-Day B.O.D. lb/day	pH
STYRENE CRACKING PLANT WASTE SUMP EFFLUENT, SAMPLING POINT NO.12 8 hour composite (increment each hour)												
June 16	0.71	400	800	8.6	9.6	284	568	224	1325	>260	>1540	6.6
June 17	0.71	200	1600	7.6	10.6	142	1136	368	2176	482	2850	6.5
Average	0.71	280	1100	8.1	10.1	200	780	300	1750	>370	>2200	
STYRENE PURIFICATION PLANT HOTWELLS EFFLUENT, SAMPLING POINT NO.S4 8 hour composite (increment each hour)												
June 16	0.45	800	800	9.6	9.6	360	360	62.3	234	45.8	172	6.3
June 17	0.45	200	200	7.6	7.6	90	90	122.3	458	19.0	71	5.5
Average	0.45	390	390	8.6	8.6	180	180	92	350	32	120	
AERATOR INFLUENT - SAMPLING POINT NO. 8 24 hour composite (increment each hour)												
May												
14-15	1.487	16,000	-	14.0	-	23,790	-	885	10,960	236	2,920	6.6
15-16	1.425	64,000	-	16.0	-	91,200	-	723	8,580	406	4,820	6.7
18-19	1.429	32,000	-	15.0	-	45,730	-	790	9,400	230	2,740	7.2
19-20	1.487	4,000	-	12.0	-	5,950	-	428	5,300	225	2,790	6.7
25-26	1.260	16,000	-	14.0	-	20,160	-	447	4,690	298	3,130	4.3
26-27	1.213	16,000	-	14.0	-	19,410	-	884	8,930	660	6,670	3.7
27-28	1.320	4,000	4,000	12.0	12.0	5,280	5,280	564	6,200	306	3,360	4.2
28-29	1.487	3,200	3,200	11.6	11.6	4,760	4,760	595	7,370	268	3,320	7.3

TABLE B-1 - SUMMARY OF DAILY ANALYSES

STYRENE OPERATIONS - CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS, DAILY VALUES Cont'd-3

Chemical Division
Koppers Company
Kobuta, Pennsylvania

Date 1952	Flow MGD	Threshold Odor Number		pO		Weighted Odor (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-day B.O.D.		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	
AERATOR INFLUENT - SAMPLING POINT NO. 8 8 hour composite (increment each hour)												
June 9	1.641	3,200	12,800	11.6	13.6	5,250	21,000	435	5,950	319	4,360	4.9
June 10	1.571	1,600	3,200	10.6	11.6	2,510	5,020	378	4,950	298	3,900	7.2
June 11	1.541	800	3,200	9.6	11.6	1,230	4,930	343	4,400	285	3,660	6.9
June 12	1.609	1,600	1,600	10.6	10.6	2,570	2,570	302	4,050	257	3,440	7.4
Average	1.46	6,250	3,600	12.6	11.8	9,130	5,260	564	6,730	316	3,760	-
Recirculation	1.524	5,400	3,800	12.4	11.9	8,250	5,800	535	6,698	282	3,579	
No "	1.32	7,600	3,600	12.9	11.8	10,100	4,750	622	6,797	383	4,120	
OIL CRACKING WASTE TO BUDATIENE WASTE OIL SKIMMER, SAMPLING POINT NO. 56 8 hour composite (increment each hour)												
June 9	0.216	16,000	16,000	14	14	3,456	3,456	22,030	39,638	11,100	19,972	8.3
June 10	0.216	64,000	256,000	16	18	13,824	55,296	13,360	24,038	8,860	15,942	7.0
June 11	0.216	80,000	160,000	16.3	17.3	17,280	34,560	12,560	22,599	7,600	13,674	6.3
June 12	0.216	80,000	80,000	16.3	16.3	17,280	17,280	15,680	28,213	9,633	17,332	7.0
Average	0.216	49,200	86,000	15.6	16.4	10,600	18,600	15,900	28,600	9,300	16,700	-

TABLE B-1 - SUMMARY OF DAILY ANALYSES

STYRENE OPERATIONS - CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS, DAILY VALUES Cont'd-4

Chemical Division
Koppers Company
Kobuta, Pennsylvania

Date 1952	Flow MGD	Threshold Odor Number		pO		Weighted Odor (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-Day B.O.D.		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	
BENZENE PLANT AREA, SAMPLING POINT NO. 42 **8 hour composite (increment each hour)**												
June 2	1.22	64	128	6.0	7.0	78	156	14.3	145	5.9	60	6.9
June 3	0.43	40	40	5.3	5.3	17	17	81.4	292	54.0	193	7.0
Average	0.82	49	74	5.6	6.2	40	61	48	220	30	130	-
BENZENE-STYRENE PURIFICATION PLANT AREAS, SAMPLING POINT NO. 38 **8 hour composite (increment each hour)**												
June 16	2.31	32	32	5	5	73.9	73.9	16.8	323	1.12	21.6	6.5
June 17	2.31	16	16	4	4	37.0	37.0	20.4	393	4.96	95.4	6.2
Average	2.31	23	23	4.5	4.5	53	53	19	360	3.0	58	-
ACETYLENE REMOVAL UNIT YARD LEVEL SUMP DISCHARGE, SAMPLING POINT NO.1 **8 hour composite (increment each hour)**												
June 4	1.09	4	8	2	3	4.36	8.72	5.1	46.3	1.64	14.90	6.6
June 5	1.09	4	2	2	1	4.36	2.18	3.1	28.2	-	-	6.7
						Grab Sample						
June 20	1.09	-	-	-	-	-	-	-	-	0.90	8.17	-
Average	1.09	4	4	2	2	4.4	4.4	4	37	1.3	11.5	-

TABLE B-1 - SUMMARY OF DAILY ANALYSES

STYRENE OPERATIONS-CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS, DAILY VALUES Cont'd-5

Chemical Division
Koppers Company
Kobuta, Pennsylvania

ETHYLENE PLANT AREA, SAMPLING POINT NO. 36
8 hour composite (increment each hour)

Date 1952	Flow MGD	Threshold Oder Number		pO		Weighted Oder (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-Day B.O.D.		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	
June 4	2.07	256	512	8.0	9.0	530	1060	47.4	817	9.3	160	6.5
June 5	2.07	3200	1600	11.6	10.6	6620	3310	30.5	526	4.5	78	6.7
June 18	2.07	400	800	8.6	9.6	828	1660	>189(1)	>3260(1)	184	3170	6.3
June 19	2.07	1600	1600	10.6	10.6	3310	3310	92.0	1590	44	759	6.4
Average	2.07	830	1020	9.7	10	1720	2110	57	980	60	1040	6.3-6.7

(1) Not included in average

ACETYLENE REMOVAL, ETHYLENE PLANT, ETHYLENE RECOVERY, AND ETHYLBENZENE PLANT AREAS, SAMPLING POINT NO.33
8 hour composite (increment each hour)

Date 1952	Flow MGD	Threshold Oder Number		pO		Weighted Oder (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-Day B.O.D.		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	
June 4	10.52	533	533	9.1	9.1	5607	5607	121.0	10600	34.3	3000	6.5
June 5	10.52	200	200	7.6	7.6	2104	2104	52.7	4618	20.3	1780	6.6
June 18	10.52	100	100	6.6	6.6	1052	1052	32.5	2850	17.2	1510	6.5
June 19	10.52	200	100	7.6	6.6	2104	1052	38.5	3370	20.1	1760	6.4
Average	10.52	210	180	7.7	7.5	2210	1890	61	5360	23	2010	6.4-6.6

TABLE B-1 - SUMMARY OF DAILY ANALYSES

STYRENE OPERATIONS - CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS, DAILY VALUES Cont'd-6

Chemical Division
Koppers Company
Kobuta, Pennsylvania

Date 1952	Flow MGD	Threshold Odor Number		pO		Weighted Odor (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-Day B.O.D.		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	
STYRENE PURIFICATION AREA, SAMPLING POINT NO.R 8 hour composite (increment each hour)												
June 2	13.4	128	256	7	8	1715	3430	25.5	2846	6.08	679	6.6
June 3	13.4	32	32	5	5	429	429	12.8	1429	8.32	929	6.7
Average	13.4	64	90	6	6.5	860	1210	19	2140	7.3	800	-
STYRENE CRACKING AREA, SAMPLING POINT NO.Q 8 hour composite (increment each hour)												
June 2	11.4	12.5	6.25	3.6	2.6	142	71	6.5	617	1.00	95	6.7
June 3	11.4	8.0	8.0	3.0	3.0	91	91	7.7	731	2.76	262	6.5
Average	11.4	9.9	7	3.3	2.8	110	80	7	670	1.9	180	-
STYRENE CRACKING AREA, SAMPLING POINT NO.37 8 hour composite (increment each hour)												
June 3	5.68	33	33	5.0	5.0	187.0	187.0	10.2	483	0.92	43.5	6.5
June 3	5.68	4.2	4.2	2.1	2.1	23.9	23.9	11.5	544	1.64	77.6	7.0
Average	5.68	12	12	3.6	3.6	68	68	11	510	1.3	61	-
OIL CRACKING AND POLYSTYRENE WASTES TO RACCOON CREEK, SAMPLING POINT NO.V 8 hour composite (increment each hour)												
June 4	8.4	25	12.5	4.6	3.6	210	105	3.1	217	6.05	423	6.4
June 5	8.4	16	16	4.	4.	134	134	13.2	924			6.9
June 20	8.4	Grab sample								2.96	207	
Average	8.4	20	14	4.3	3.8	168	118	8	570	4.5	320	

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SECTION C - WASTE LINES AND TREATMENT

There are six outfall waste lines discharging into the Ohio River, namely: main outfall, lagoon effluent, 30 in. outfall to Raccoon Creek, 18 in. outfall to Raccoon Creek, 8 in. outfall to Raccoon Creek, and phthalic anhydride plant effluent. The lagoon effluent and the outfalls to Raccoon Creek discharge to Raccoon Creek, which in turn flows into the Ohio River.

Plant wastes have been placed in two categories: contaminated (concentrated), and uncontaminated (dilute). The so-called contaminated wastes are considered to contain enough waste constituents to justify treatment. The uncontaminated wastes are relatively dilute and consist for the most part of cooling water. The sanitary wastes flow through an Imhoff tank before discharging into Raccoon Creek. The waste line systems are shown in Figures C-1 and C-2. The phthalic anhydride plant is independent of the butadiene and styrene plants and is located in an entirely different area.

DISCUSSION OF WASTE SYSTEMS

1. Contaminated Wastes

There are two separate contaminated waste systems, one for the butadiene units, the other for the styrene plant. Certain oily wastes from the oil cracking unit of the styrene plant are treated in the butadiene waste treatment units.

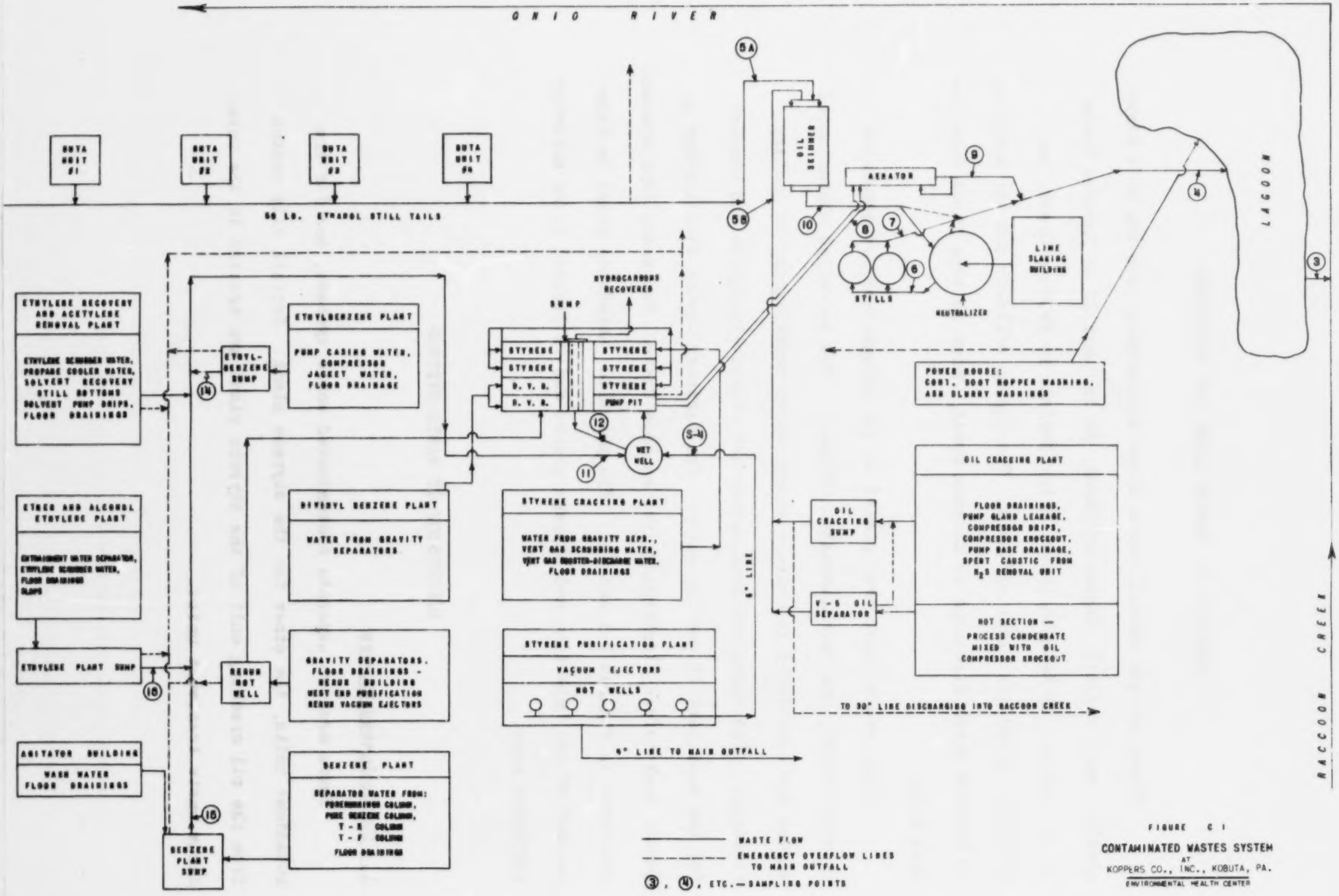
OHIO RIVER
BUTA UNIT #1
BUTA UNIT #2
BUTA UNIT #3
BUTA UNIT #4
50 LB. ETHANOL STILL TAILS
5A
5B
OIL SKIMMER
10
AERATOR
9
8
7
6
STILLS
NEUTRALIZER
LIME SLAKING BUILDING
14
LAGOON
3
RACCOON CREEK
ETHYLENE RECOVERY AND ACETYLENE REMOVAL PLANT
ETHYLENE SCRUBBER WATER, PROPANE COOLER WATER, SOLVENT RECOVERY STILL BOTTOMS SOLVENT PUMP DRIPS, FLOOR DRAININGS
ETHYLBENZENE SUMP
IN
ETHYLBENZENE PLANT
PUMP CASING WATER, COMPRESSOR JACKET WATER, FLOOR DRAINAGE
SUMP
HYDROCARBONS RECOVERED
STYRENE
STYRENE
D. V. B.
D. V. B.
STYRENE
STYRENE
STYRENE
PUMP PIT
12
11
HOT WELL
S-II
POWER HOUSE: CONT. SOOT HOPPER WASHING, ASH SLURRY WASHINGS
ETHER AND ALCOHOL ETHYLENE PLANT
ENTRAINMENT WATER SEPARATOR, ETHYLENE SCRUBBER WATER, FLOOR DRAININGS FLAPS
DIVINYL BENZENE PLANT
WATER FROM GRAVITY SEPARATORS
STYRENE CRACKING PLANT
WATER FROM GRAVITY SEPS., VENT GAS SCRUBBING WATER, VENT GAS BOOSTER-DISCHARGE WATER, FLOOR DRAININGS
6" LINE
OIL CRACKING PLANT
FLOOR DRAININGS, PUMP GLAND LEAKAGE, COMPRESSOR DRIPS, COMPRESSOR KNOCKOUT, PUMP BASE DRAINAGE, SPENT CAUSTIC FROM H_2S REMOVAL UNIT
HOT SECTION — PROCESS CONDENSATE MIXED WITH OIL COMPRESSOR KNOCKOUT
OIL CRACKING SUMP
V-5 OIL SEPARATOR
ETHYLENE PLANT SUMP
16
REBUN HOT WELL
GRAVITY SEPARATORS, FLOOR DRAININGS - REBUN BUILDING WEST END PURIFICATION REBUN VACUUM EJECTORS
STYRENE PURIFICATION PLANT
VACUUM EJECTORS
HOT WELLS
TO 30" LINE DISCHARGING INTO RACCOON CREEK
6" LINE TO MAIN OUTFALL
AGITATOR BUILDING
WASH WATER FLOOR DRAININGS
15
BENZENE PLANT SUMP
BENZENE PLANT
SEPARATOR WATER FROM: FORERUNNINGS COLUMN, PURE BENZENE COLUMN, T-E COLUMN T-F COLUMN FLOOR DRAININGS
WASTE FLOW
EMERGENCY OVERFLOW LINES TO MAIN OUTFALL
③, ⑭, ETC.—SAMPLING POINTS

FIGURE C 1

CONTAMINATED WASTES SYSTEM
AT
KOPPERS CO., INC., KOBUTA, PA.
ENVIRONMENTAL HEALTH CENTER

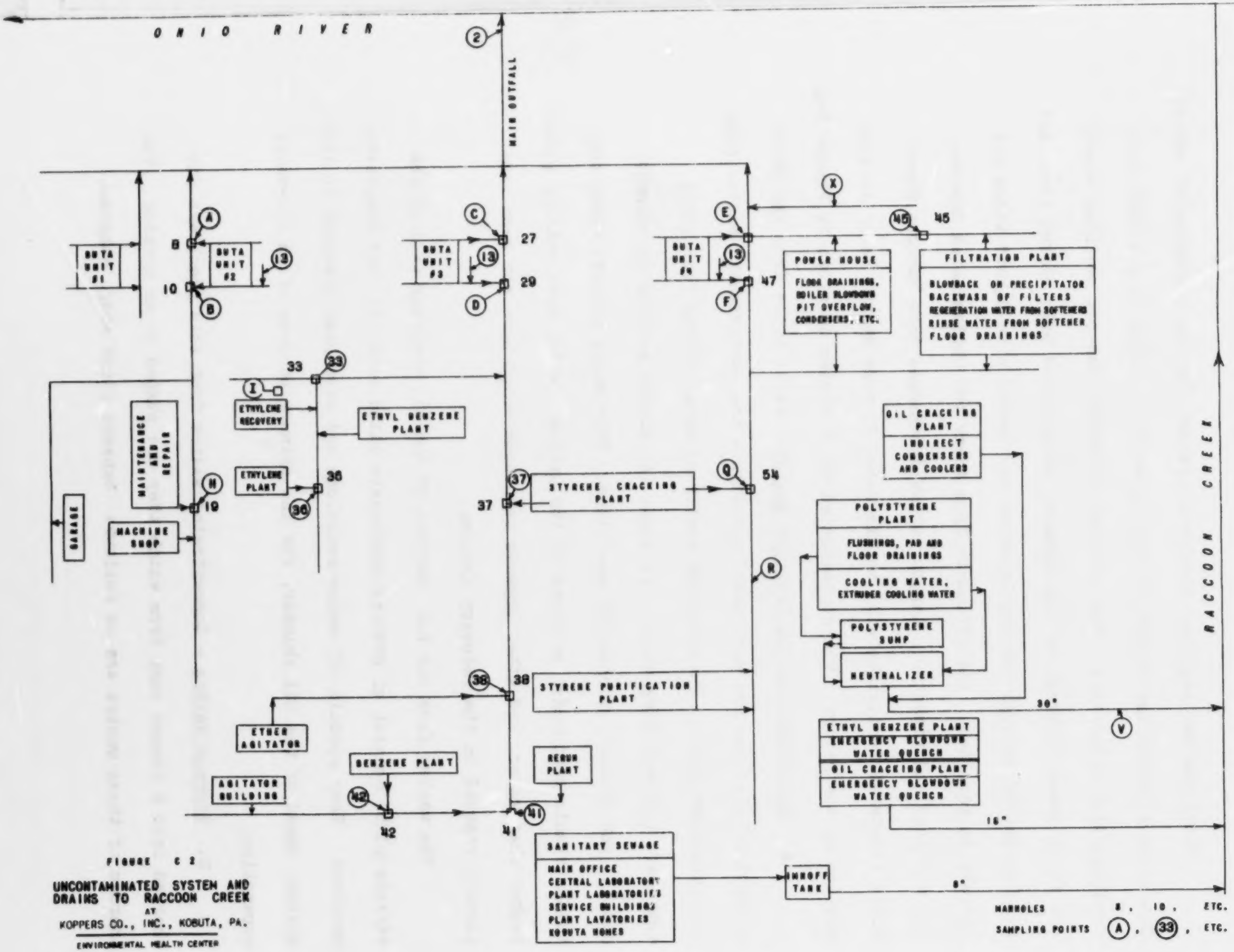
OHIO RIVER
2
MAIN OUTFALL
BUTA UNIT #1
BUTA UNIT #2
BUTA UNIT #3
BUTA UNIT #4
A
B
8
10
13
C
D
27
29
E
F
47
X
45
POWER HOUSE
FLOOR DRAININGS, BOILER BLOWDOWN PIT OVERFLOW, CONDENSERS, ETC.
FILTRATION PLANT
BLOWBACK ON PRECIPITATOR
BACKWASH OF FILTERS
REGENERATION WATER FROM SOFTENERS
RINSE WATER FROM SOFTENER
FLOOR DRAININGS
33
I
ETHYLENE RECOVERY
ETHYL BENZENE PLANT
ETHYLENE PLANT
36
MAINTENANCE AND REPAIR
H
19
GARAGE
MACHINE SHOP
37
STYRENE CRACKING PLANT
Q
54
R
OIL CRACKING PLANT
INDIRECT CONDENSERS AND COOLERS
POLYSTYRENE PLANT
FLUSHINGS, PAD AND FLOOR DRAININGS
COOLING WATER, EXTRUDER COOLING WATER
POLYSTYRENE SUMP
NEUTRALIZER
38
STYRENE PURIFICATION PLANT
30"
V
ETHER AGITATOR
BENZENE PLANT
AGITATOR BUILDING
42
41
RERUN PLANT
ETHYL BENZENE PLANT
EMERGENCY BLOWDOWN WATER QUENCH
OIL CRACKING PLANT
EMERGENCY BLOWDOWN WATER QUENCH
16"
SANITARY SEWAGE
MAIN OFFICE
CENTRAL LABORATORY
PLANT LABORATORIES
SERVICE BUILDINGS
PLANT LAVATORIES
KOBUTA HOMES
IMHOFF TANK
8"
RACCOON CREEK
MANHOLES 8, 10, ETC.
SAMPLING POINTS (A), (33), ETC.

FIGURE C 2

UNCONTAMINATED SYSTEM AND DRAINS TO RACCOON CREEK
AT
KOPPERS CO., INC., KOBUTA, PA.

ENVIRONMENTAL HEALTH CENTER

There are two separate treatment systems for the contaminated wastes. The styrene wastes are passed through an aerator, which is provided with recirculation facilities. The combined butadiene and oil cracking wastes are first passed through an oil skimmer, neutralized with slaked lime, and finally passed through two stills, which are heated with direct steam and operate in parallel. The effluents from these two contaminated systems are combined and piped to a lagoon, which discharges into Raccoon Creek. Waste treatment facilities will be discussed in more detail later in this section of the report. The contaminated waste system is shown in Figure C-1.

A. Butadiene and Oil Cracking Wastes - Still tails from the 50-lb ethanol stills (two for each unit) constitute the contaminated wastes from the butadiene plant. They consist mostly of water coming from three sources: (1) scrubbing water, (2) steam for direct heating in columns, and (3) end product of chemical reactions. This waste process water contains organic compounds, produced in the process, which have boiling points higher than water, and other organic compounds which have not been completely removed in the recovery systems.

The wastes from the hot section of the oil cracking unit of the styrene plant consist of process condensate mixed with oil, and compressor knockout. They contain oil-water emulsions and have been diverted to this system, ahead of the oil skimmer, for the primary purpose of an oil-water separation.

B. Styrene Wastes - Concentrated wastes from this plant are discharged into a common sump from which they are pumped to an aerator. The sources of these wastes are as follows: benzene plant sump, ethylene plant sump, ethylbenzene sump, styrene cracking sump (5 sections), divinyl benzene sump (2 sections), ethylene recovery and acetylene removal plant, and styrene purification hot wells.

2. Uncontaminated Wastes (See Figure C-2)

A. Wastes Flowing to Main Outfall - These wastes represent the major volume of wastes from the Kobuta plant. They originate in all plant areas (phthalic anhydride excepted) and include storm water and maintenance area drainage.

B. Outfall Lines to Raccoon Creek

1. Thirty-inch line - These wastes include those from the polystyrene plant and cooling water from the oil cracking plant.

2. Eighteen-inch line - These wastes consist of quench water for emergency blowdowns from the ethylbenzene and oil cracking plants. There is no normal routine blowdown of any product or by-product into this line. At the ethylbenzene plant, the relief valves from three stills and the conversion systems are tied into the line leading to the emergency blowdown sump. At the oil cracking plant, the relief valves from the various stills and scrubbers tie into this line. Some purge steam is bled continuously into the line, with a flow of 20-30 gpm of water being maintained on the cascade trays in the base of the stack.

3. Eight-inch line - This carries sanitary sewage in the form of effluent from an Imhoff tank.

3. Phthalic Anhydride Wastes

A. Dilute Wastes - These wastes consist essentially of cooling water and are discharged directly into a ditch which drains into the Ohio River about 300 ft above the Kobuta, river pumping station.

B. Concentrated Wastes - These wastes are discharged into a series of lagoons whose capacity is supposed to prevent overflow. The retaining walls of the last two units were too porous, at the time of the survey, to prevent seepage into the drainage ditch for the dilute wastes. It will be necessary to plug the pores of these lagoon walls with compact materials in order to prevent leakage directly to the river.

DISCUSSION OF WASTE TREATMENT

There are two separate waste treatment systems for the contaminated wastes, one for the styrene wastes, the other for the butadiene and oil cracking wastes.

4. Styrene Waste Treatment

All of the combined, concentrated wastes from the styrene units, with the exception of process wastes from the oil cracking plant, are pumped from a wet well to a four-cell, wooden "Fluor-Aerator," which is 24' x 48' x 22' deep. Each cell of the aerator is 24' x 12' in cross section and filled with wooden slats, serving as baffles. Wastes are distributed to each cell from a common header at a distance of about 15' from the ground. There are 42 ~~spray nozzles~~ (10 ~~in each end~~ cell and 11 in each center cell) and the sprayed wastes fall down through the aerator, countercurrent to air blown up through the tower. There is an air blower in the outside wall of each cell, at the base of the aerator, each one having a capacity of 91,200 cu ft/min.

Two variable capacity, centrifugal pumps, operating in parallel, are provided for recirculation. Each has a capacity of 1000 gpm at 40' head. They draw suction from a collection basin, at one end of the aerator, and discharge through a common line to sprays in each cell (12/cell). Recirculation is estimated to be approximately 1400 gpm. There is an approximate temperature drop in the wastes of 19°C (37° to 18°) in passing through the aerator.

5. Butadiene and Oil Cracking Waste Treatment

A. Oil Skimmer (See Figure C-3) - The concentrated wastes from the butadiene units (50 lb ethanol still tails) and the oil cracking unit (effluents from V-5 oil separator and oil cracking sump) are first discharged into one end of an oil skimmer. An oil-water separation is made, with the oil being drawn off for fuel purposes and the water layer being discharged to a neutralizing tank. The effective capacity of the oil skimmer is approximately 205,000 gallons. With a flow of 1055 gpm (1.52 MGD), the theoretical detention time would be 3-1/4 hours.

B. Neutralizer - Slaked lime is added to the water layer effluent from the oil skimmer as it flows into the base of a neutralizing tank. During the period of the survey, the pH of the influent ranged from 4.4 to 4.6, while the pH range of the effluent was 5.7 to 11.4.

The neutralizing tank is a cylindrical concrete tank, radius 5' 4",

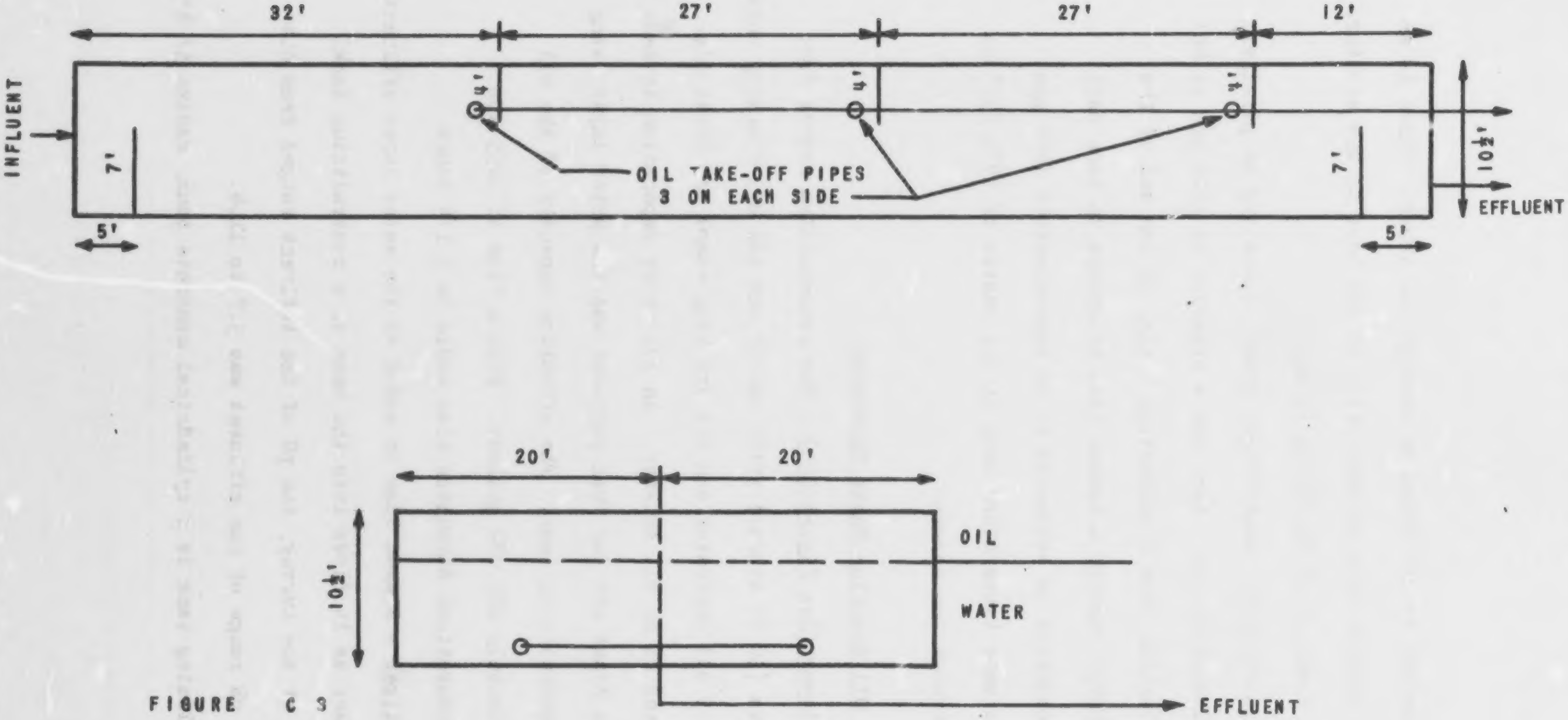
32'
27'
27'
12'
INFLUENT
7'
5'
4'
4'
4'
OIL TAKE-OFF PIPES
3 ON EACH SIDE
7'
5'
10½'
EFFLUENT
20'
20'
10½'
OIL
WATER
EFFLUENT

FIGURE C 3

OIL SKIMMER
WASTE TREATMENT PLANT
AT
KOPPERS CO., INC., KOBUTA, PA.

ENVIRONMENTAL HEALTH CENTER

effective depth 8', having an effective capacity of approximately 5350 gallons. With a flow of 1055 gpm, the theoretical holding time would be approximately 5 minutes. A larger or additional tank would probably increase the efficiency of this unit. The overflow from the neutralizer is pumped to the treatment stills.

C. Treatment Stills (See Figure C-4) - A twin filter unit was originally installed in the line between the neutralizer and the still feed pumps, but was subsequently taken out of service because of operational difficulties. The two stills operate in parallel and are heated with direct steam so as to condense 3 to 5 per cent of the total wastes as overhead. The condensate is run through separators, with the water layers either being used as process water or pumped back into the oil skimmer inlet. The still tails are discharged to the lagoon along with the aerator effluent.

6. Lagoon (See Figure C-1)

The effluents from the styrene, and butadiene and oil cracking waste treatment systems are combined and discharged into a lagoon. The estimated capacity of this lagoon is 14 MG. Based on an average flow value of 2.92 MGD for the period of the survey, the theoretical holding time was 4.8 days. Short-circuiting probably occurs, however.

The inlet end of the discharge line was submerged. More wastes seeped through the walls of the lagoon than flowed through the outfall to Raccoon Creek. Gas bubbles were continually rising through the liquid, over the whole lagoon area, probably being gases of decomposition. The color of the effluent changed intermittently from light grey to black, indicating internal disturbances within the liquid in the lagoon.

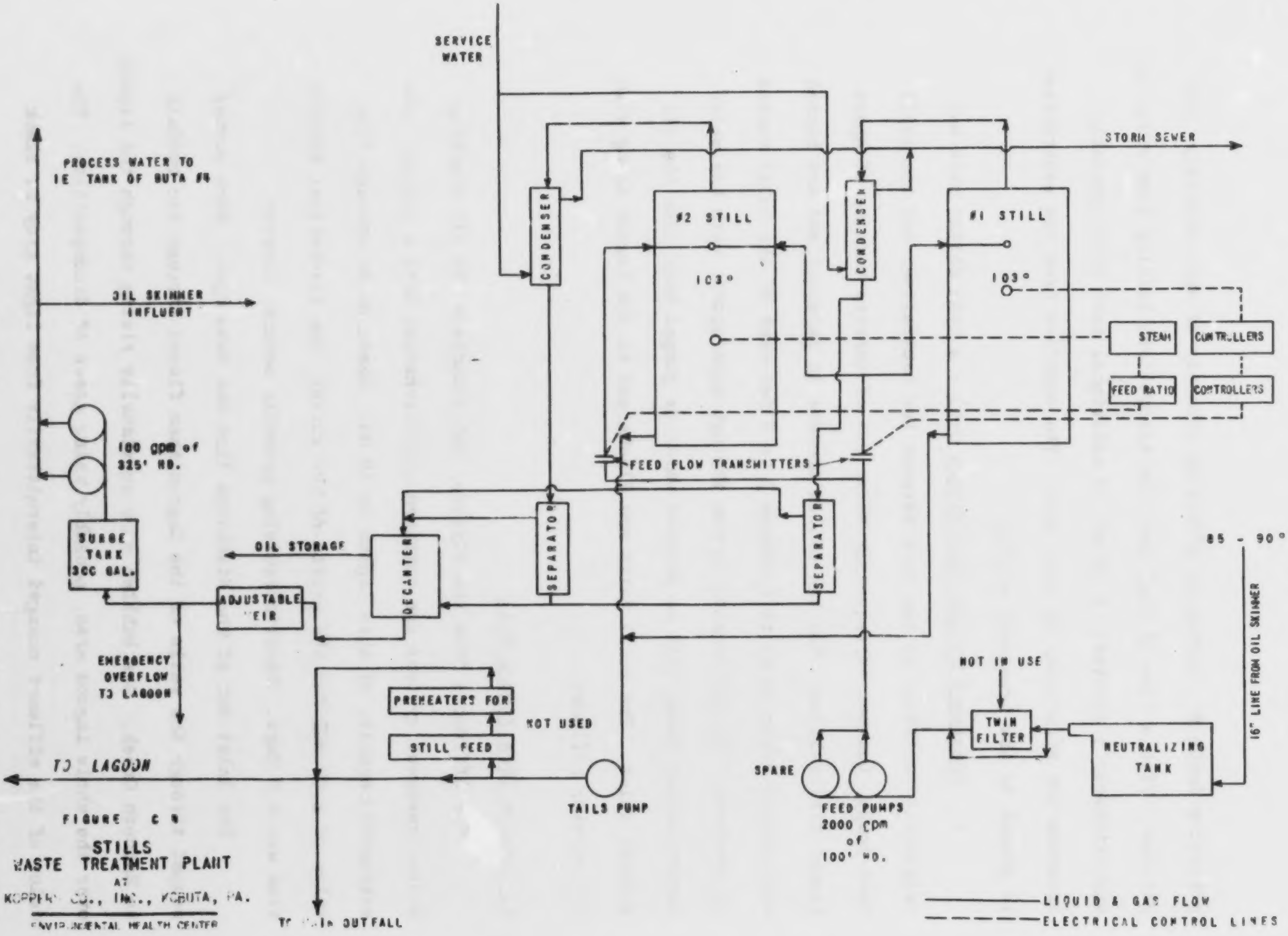
SERVICE WATER
STORM SEWER
PROCESS WATER TO 1E TANK OF BUTA #4
OIL SKIMMER INFLUENT
CONDENSER
#2 STILL
103°
CONDENSER
#1 STILL
103°
STEAM
CONTROLLERS
FEED RATIO
CONTROLLERS
100 gpm of 325' HD.
SURGE TANK 300 GAL.
FEED FLOW TRANSMITTERS
SEPARATOR
SEPARATOR
OIL STORAGE
DECANTER
ADJUSTABLE WEIR
EMERGENCY OVERFLOW TO LAGOON
85 - 90°
16" LINE FROM OIL SKIMMER
NOT IN USE
TWIN FILTER
NEUTRALIZING TANK
PREHEATERS FOR
STILL FEED
NOT USED
TO LAGOON
TAILS PUMP
SPARE
FEED PUMPS 2000 gpm of 100' HD.
TO MAIN OUTFALL
LIQUID & GAS FLOW
ELECTRICAL CONTROL LINES

FIGURE C 9

STILLS
WASTE TREATMENT PLANT
AT
KOPPERS CO., INC., KOBUTA, PA.

ENVIRONMENTAL HEALTH CENTER

SURVEY PROCEDURES

7. Sample Collection

Kobuta butadiene and styrene operations are for the most part on a continuous, 24 hr/day, basis. It was assumed that waste flows were relatively constant throughout sampling periods, and equal sample increments were taken at each sampling point.

The raw river water intake, the main outfall, and the lagoon influent and effluent, were equipped with continuous sampling devices during all or part of the sampling period. During periods when these devices were not functioning, samples at these points were collected manually. All other samples were taken manually.

The following tabulation shows the sampling schedule for all samples not already discussed in the butadiene (A) and styrene (B) sections. All samples were taken at hourly intervals and composited. Eight-hour composites were collected between the hours 8:00 AM and 4:00 PM.

	Station Number	Hours Composited	Days Sampled
A. Raw water intake and outfalls:			
1. Raw water intake	1	24	22
2. Main outfall	2	24	22
3. Lagoon outfall	3	24	22
4. Oil cracking and polystyrene outfall to Raccoon Creek	V	8	2
5. Phthalic anhydride	W4	8	2

	Station Number	Hours Composited	Days Sampled
B. Waste treatment units:			
1. Lagoon influent	4	24	7
		8	5
2. Oil skimmer influent	5	24	7
		8	1
3. Butadiene waste to oil skimmer	5a	8	4
4. Oil cracking waste to oil skimmer	5b	8	4
5. Oil skimmer effluent	10	8	4
6. Neutralized still feed	6	24	8
		8	4
7. Still tails	7	24	8
		8	4
8. Aerator influent	8	24	8
		8	4
9. Aerator effluent	9	24	8
		8	4
C. Miscellaneous wastes:			
1. Ash sluicing line from power house to main outfall	45	8	2
2. Storage and maintenance area	H2	4	1
		8	1
3. Condenser water from waste treatment stills (to main outfall)	X	8	2

(See Figure C-1 and Figure C-2 for location of sampling points).

Samples of Group A are intended to indicate the character of wastes being discharged to the Ohio River. Samples of Group B are intended to show the effectiveness of waste treatment facilities. Samples of Group C show the character of certain wastes within the plant area.

Separate samples were collected for the phenol and oil determinations. The phenol samples were preserved by adding approximately 4 grams of copper sulfate to gallon bottles before sampling. The oil samples were collected in separate glass-stoppered bottles and all of the contents analyzed.

8. Flow Measurements

(1) Raw river water intake - There were two discharge lines from the pumping station, with a 54 in. Venturi meter in each one. Daily flow records were obtained from Koppers records.

(2) Main outfall - Flow equal to sum of raw river water intake and well water used, minus sum of other outfalls (11 calculable).

(3) Lagoon effluent and influent - These flows were assumed equal. Influent is sum of treated wastes from butadiene and styrene plants.

(4) Oil cracking and polystyrene wastes to Raccoon Creek - Estimated from metered water usage.

(5) Phthalic anhydride effluent - This was estimated from metered water usage.

(6) Oil skimmer influent and effluent - The influent is the sum of butadiene and oil cracking wastes to this unit. Effluent, the same.

(7) Butadiene waste to oil skimmer - This flow was measured with a recording orifice meter.

(8) Oil cracking waste to oil skimmer - This flow was estimated from metered water usage.

(9) Neutralized still feed - This was assumed to be the same as the oil skimmer effluent.

(10) Still tails - This flow was estimated, knowing the neutralizer effluent flow, the steam feed to the stills (direct heat), and still operations. It was equal to the still feed plus steam feed, minus 4 per cent of total wastes, and was calculated to be 4-1/2 per cent greater than the still feed.

(11) Aerator influent and effluent. These were assumed to be the same. Orifice meter records were available for the influent.

(12) The miscellaneous waste flows were estimated from metered water usage records.

9. Laboratory Analyses

The following laboratory determinations were made on samples:

(1) Threshold odor number (hot and cold).

(2) pO values (hot and cold); calculated from threshold odor number values. Fractional, rather than whole, numbers were used to point out small differences.

(3) Oxygen consumed from dichromate.

(4) 5-day B.O.D.

(5) pH.

(6) Phenols.

(7) Oils.

The procedures followed in making threshold odor number, B.O.D., and pH determinations were those given in "Standard Methods for the Examination of Water and Sewage," 9th Edition.(1) The dilution technic for threshold odor was not followed. Successive dilution ratios, with odor-free water, of 2:1, were used in order to conform to the physiological Weber-Fechner law, that is, each successive dilution was one-half that of the previous one. The procedures for the other determinations are given in the appendix at the end of this report.

10. Explanation of Laboratory Analyses

A brief explanation of the various laboratory determinations is given in the appendix at the end of this report, and is intended to serve as an aid in the interpretation of the analytical results reported.

DISCUSSION OF RESULTS

Butadiene and styrene wastes have been discussed in Sections A and B of this report. The results of daily analyses of samples taken in these areas have been given in tables in the respective sections. The results of daily analyses of samples taken in other parts of the wastes systems are given in Table C-1.

11. Uncontaminated Systems (See Figure C-2)

Most of the relatively dilute wastes are discharged to the main outfall, with minor quantities being discharged to Raccoon Creek through small lines, and to the Ohio River from the phthalic anhydride plant.

A. Main Outfall

1. **Butadiene wastes** - The average daily quantities of waste constituents discharged to the main outfall are as follows:

	Quantities Gross	 Net
Weighted threshold odor (cold) (1)	45,950	43,500
Oxygen consumed ($K_2Cr_2O_7$), lb/day	24,600	5,700
5-day B.O.D., lb/day	5,480	3,850

(1) Empirical quantitative values obtained by multiplying odor values by flows in MGD.

The average volume of wastes was 63.7 MGD.

2. Styrene wastes - The average daily quantities of waste constituents discharged to the main outfall are as follows:

	Quantities Gross	 Net
Weighted threshold odor		
Cold	3,300	2,530
Hot	3,300	2,440
Oxygen consumed ($K_2Cr_2O_7$), lb/day	9,330	7,020
5-day B.O.D., lb/day	3,270	2,780

The average volume of wastes was 43.3 MGD.

3. Miscellaneous wastes - Three additional waste lines (other than butadiene and styrene wastes), discharging to the main outfall, were sampled during the period of the survey.

a. Condenser water from waste treatment stills (Sampling Point X). The average concentrations and daily quantities of waste constituents, discharged at this point, are as follows:

Still Condenser Water

	Concentrations	Quantities Gross	Quantities Net
Threshold odor number			
Cold	8	39	29
Hot	16	78	34
pO			
Cold	3		
Hot	4		
Oxygen consumed ($K_2Cr_2O_7$),	4.4 ppm	180 lb/day	0 lb/day
5-day B.O.D.	1.2 ppm	50 lb/day	16 lb/day
pH	6.7 - 6.8		

The average flow during the sampling period was 4.87 MGD.

b. Emergency line at powerhouse, for ash sluicing wastes (Sampling Point 45). The flow in this line was negligible, so quantities of waste constituents were not calculated. The average concentrations of waste constituents discharged in this line are as follows: cold threshold odor number, 11; hot threshold odor number, 23; cold pO, 3.5; hot pO, 4.5; oxygen consumed from dichromate, 85 ppm; 5-day B.O.D., 49 ppm; and the pH range, 7.8 - 7.9.

c. Storage and maintenance area (Sampling Point #42). The average concentrations of waste constituents in this waste line are as follows: cold threshold odor number, 2020; hot threshold odor number, 2020; cold pO, 11.1; hot pO, 11.1; oxygen consumed from dichromate, 2520 ppm; 5-day B.O.D., 180 ppm; and the pH range, 7.2 - 7.4.

The flow in this line was also negligible, so quantities of waste constituents were not calculated.

4. Total wastes to main outfall - The total flows, based on sampling points in the systems, are as follows:

	Flow MGD	Per Cent of Total
Butadiene plant	63.7	57
Styrene plant	43.3	39
Miscellaneous	4.9	4
Total	111.9	100

The total calculated average flow in the main outfall was actually 127 MGD, during the period of the survey.

The average, total net quantities of waste constituents discharged daily to the main outfall are as follows:

	Total Net Quantities		Per Cent of Total (2)		
	A(1)	B(2)	Butadiene	Styrene	Misc.
Weighted threshold odor (cold)	20,000	46,100	94	6	< 1
Oxygen consumed ($K_2Cr_2O_7$), lb/day	7,400	12,700	45	55	0
5-day B.O.D., lb/day	4,460	6,650	58	42	< 1

(1) Actual values obtained at main outfall.
(2) Values obtained at sampling points within plant.

B. Other Outfalls

1. Thirty-inch line to Racoon Creek (Sampling Point V) - The wastes in this line consist of cooling water from the oil cracking plant and flushings, pad and floor drainings, process cooling water, and extruder cooling water from the polystyrene plant. The volumes from each

plant are known but the concentrations of waste constituents are not. The concentrations of waste constituents in the cooling water from the oil cracking plant are probably low, and it might be assumed that the bulk of the waste constituents come from the polystyrene plant.

The average daily concentrations and quantities of waste constituents discharged in this line are as follows:

	Concentrations	Quantities	
		Gross	Net
Threshold odor number			
Cold	20	170	150
Hot	14	120	44
pO			
Cold	4.3		
Hot	3.8		
Oxygen consumed ($K_2Cr_2O_7$)	8 ppm	570 lb/day	0 lb/day
5-day B.O.D.	4.5 ppm	320 lb/day	260 lb/day
pH	6.4 - 6.9		

The average flow was estimated to be 8.4 MGD

2. Eighteen-inch outfall to Racoon Creek - Water from the emergency blowdown sump for the ethylbenzene and oil cracking plants constituted the wastes in this line. The flow was relatively insignificant and samples were not taken.

3. Eight-inch line to Racoon Creek - This waste line was not sampled. It carried sanitary wastes from the plant (1350 employees) and Kobuta Village (approximately 500 people). The sanitary sewage flowed through an Imhoff tank to Racoon Creek. The digested sludge was pumped onto sand drying beds, with the effluent discharging back into the outfall line.

4. Phthalic anhydride plant outfall (Sampling Point W4) - The average concentrations and daily quantities of waste constituents discharged into this line are as follows:

	Concentrations	Quantities	
		Gross	Net
Threshold odor number			
Cold	16	48	30
Hot	23	69	33
pO			
Cold	4.		
Hot	4.5		
Oxygen consumed ($K_2Cr_2O_7$)	36 ppm	910 lb/day	580 lb/day
5-day B.O.D.	13 ppm	330 lb/day	240 lb/day
pH	6.3 - 6.4		

The average flow was estimated to be 3. MGD.

During the sampling period, the concentrated wastes (approximately 30 GPM) were not being discharged to this outfall but sent to lagoons, and this was stated to simulate normal conditions. However, some of these wastes were seeping through the lagoon walls to this outfall and may well have influenced the character of the raw water (Ohio River intake). Samples from sampling point W-4 include any effects of this seepage contamination.

12. Contaminated Systems (See Figure C-1)

All of the so-called contaminated (concentrated) wastes are discharged to treatment facilities, before being discharged to Raccoon Creek. The butadiene and oil cracking wastes go to one treatment system, while the styrene wastes go to another. These waste treatment facilities will be discussed in more detail later in this section.

A. Butadiene Wastes - The average daily concentrations and quantities of waste constituents discharged to this waste system are as follows:

	Concentrations	Quantities	
		Gross	Net
Threshold odor number			
Cold	23,000	22,500	22,500
Hot	56,600	55,500	55,500
pO			
Cold	14.5		
Hot	15.8		
Oxygen consumed ($K_2Cr_2O_7$)	9,050 ppm	73,800 lb/day	73,600 lb/day
5-day B.O.D.	4,700 ppm	38,300 lb/day	38,300 lb/day
pH	3.8 - 4.0		

The average volume of wastes was 0.98 MGD.

B. Styrene Wastes - The average daily quantities of waste constituents discharged to this system are as follows:

	Quantities	
	Gross	Net
Weighted threshold odor		
Cold	19,700	19,700
Hot	23,800	23,800
Oxygen consumed ($K_2Cr_2O_7$)	35,300 lb/day	35,000 lb/day
5-day B.O.D.	20,500 lb/day	20,400 lb/day

The average volume of wastes was 1.68 MGD.

13. Waste Treatment

A. Treatment System for Contaminated Wastes from Butadiene Plant and Oil Cracking Unit of Styrene Plant - The daily analyses of samples and quantities of waste constituents are given in Table C-1.

1. Oil Skimmer - This unit is shown in Figure C-3. The average concentrations of waste constituents entering and leaving the oil skimmer are as follows:

	Influent	Effluent
Threshold odor number		
Cold	26,400	18,700
Hot	60,500	23,000
pO		
Cold	14.7	14.2
Hot	15.9	14.5
Oxygen consumed ($K_2Cr_2O_7$), ppm	10,300	7,890
5-day B.O.D., ppm	5,530	4,840
pH	3.2 - 4.3	4.4 - 4.6

The oil skimmer effluent was sampled during the period June 9 through June 12. The influent values are averages for the butadiene and oil cracking wastes to the oil skimmer during the same time period.

The average daily quantities and removals of waste constituents in the oil skimmer are as follows:

	Influent	Effluent	Removal	Per Cent Removal
Weighted threshold number				
Cold	31,500	22,400	9,100	29
Hot	72,600	27,600	45,000	62
Oxygen consumed ($K_2Cr_2O_7$), lb/day	103,000	78,600	24,400	24
5-day B.O.D., lb/day	55,300	48,200	7,100	13

The average flow during this period was 1.2 MGD.

2. Neutralizer - The average concentrations of waste constituents entering and leaving the neutralizer are as follows:

	Influent	Effluent
Threshold odor number		
Cold	18,700	23,000
Hot	23,000	20,000
pO		
Cold	14.2	14.5
Hot	14.5	14.3
Oxygen consumed ($K_2Cr_2O_7$), ppm	7,890	8,940
5-day B.O.D., ppm	4,840	4,020
pH	4.4 - 4.6	5.7 - 11.4

The average daily quantities and removals of waste constituents in the neutralizer, for the period June 9 through June 12, are as follows:

	Influent	Effluent	Removal	Per Cent Removal
Weighted threshold odor				
Cold	22,400	27,600	- 5,200(1)	-23(1)
Hot	27,600	24,000	3,600	13
Oxygen consumed ($K_2Cr_2O_7$), lb/day	78,600	89,200	-10,600(1)	-13(1)
5-day B.O.D., lb/day	48,200	40,100	8,100	17

(1) Indicates increase rather than decrease. Probably due to inherent sampling difficulties.

The average flow during this period was 1.2 MGD.

3. **Stills** - The average concentrations of waste constituents entering and leaving the stills, for the period May 14 to June 12, are as follows:

	Influent	Effluent
Threshold odor number		
Cold	17,800	3,300
Hot	18,700	5,510
pO		
Cold	14.1	12.1
Hot	14.0	12.4
Oxygen consumed ($K_2Cr_2O_7$), ppm	8,280	6,000
5-day B.O.D., ppm	3,520	2,300
pH	5.7 - 11.4	5.6 - 11.5

The average daily quantities and removals of waste constituents in the stills, for the period May 14 to June 12, are as follows:

	Influent	Effluent	Removal	Per Cent Removal
Weighted threshold odor				
Cold	25,100	4,850	20,250	81
Hot	23,600	6,180	17,420	74
Oxygen consumed ($K_2Cr_2O_7$), lb/day	95,500	73,200	22,400	23
5-day B.O.D., lb/day	40,800	28,200	12,600	31

The average influent flow was 1.41 MGD, while the average effluent flow was 1.46 MGD. Three to five per cent of the wastes are condensed as overhead and the stills (2) are direct heated with steam.

4. **Over-All Treatment Efficiency** - The average, over-all waste removal efficiencies of the units of this treatment system, for the period June 9 through June 12, are as follows:

Waste Removal Efficiencies - Per Cent

Unit	Weighted Threshold Odor		Oxygen Consumed ($K_2Cr_2O_7$)	5-Day B.O.D.
	Cold	Hot		
Oil skimmer	29	62	24	13
Neutralizer	-17(1)	5	-10(1)	15
Stills	73	24	31	30
Total	85	91	45	58

(1) Indicates increase rather than decrease.

The percentages of total waste constituents removed by the individual treatment units are as follows:

Waste Removal Efficiencies - Per Cent of Total

Unit	Weighted Threshold Odor		Oxygen Consumed ($K_2Cr_2O_7$)	5-Day B.O.D.
	Cold	Hot		
Oil skimmer	34	68	53	22
Neutralizer	-20(1)	6	-22(1)	26
Stills	86	26	69	52
Total	100	100	100	100

(1) Indicates increase rather than decrease.

B. Treatment System for Contaminated Wastes from Styrene Plant (Oil Cracking Wastes Excepted) - The average concentrations of waste constituents entering and leaving the aerator unit are as follows:

	Influent		Effluent	
	Recirculation	No Recirculation	Recirculation	No Recirculation
Threshold odor number				
Cold	5,500	7,700	670	360
Hot	3,800	3,600	240	330
pO				
Cold	12.4	12.9	9.8	8.5
Hot	11.9	11.8	7.6	8.3
Oxygen consumed ($K_2Cr_2O_7$), ppm	540	620	180	150
5-day B.O.D., ppm	280	380	84	37
pH	4.9 - 7.4	3.7 - 7.3	6.0 - 7.3	3.8 - 7.9

The average daily quantities and removals of waste constituents in the aerator are as follows:

	Influent	Effluent	Removal	Per Cent Removal
With Recirculation				
Weighted threshold odor				
Cold	8,400	1,360	7,040	84
Hot	5,800	290	5,510	95
Oxygen consumed ($K_2Cr_2O_7$), lb/day	6,700	2,320	4,380	65
5-day B.O.D., lb/day	3,580	1,080	2,500	70

Average flow was 1.52 MGD.

	Influent	Effluent	Removal	Per Cent Removal
Without Recirculation				
Weighted threshold odor				
Cold	10,200	480	9,720	95
Hot	4,750	440	4,310	91
Oxygen consumed ($K_2Cr_2O_7$), lb/day	6,800	1,680	5,120	75
5-day B.O.D., lb/day	4,120	410	3,710	90

Average flow was 1.3 MGD.

The recirculation ratio $\left(\frac{\text{recirculated volume}}{\text{volume of fresh feed}}\right)$ during the survey period was 1.55 : 1.

C. **Lagoon** - More lagoon wastes seep through the lagoon walls than are discharged to the outfall but, for practical purposes, it is assumed that samples from the outfall are representative of the lagoon effluent.

The average concentrations of waste constituents entering and leaving the lagoon are as follows:

Concentrations of Waste Constituents

	Influent	Effluent
Threshold odor number		
Cold	1,800	590
Hot	2,200	540
pO		
Cold	10.8	9.2
Hot	11.1	9.1
Oxygen consumed ($K_2Cr_2O_7$), ppm	2,950	2,010
5-day B.O.D., ppm	1,370	1,110
pH	6.2 - 11.3	6.5 - 7.2
Phenols, ppm	3.5(1)	12.8(1)
Oils, ppm	230	45

(1) See Table C-1 for summary of daily analyses.

Phenol analyses were made on only two lagoon influent samples during the period of the survey (June 9 and 11, 1952 1953). The average phenol concentration for these two days was 3.5 ppm. Lagoon effluent samples were analyzed for phenols on six different days, the average concentration being 12.8 ppm. The average phenol concentration in the lagoon effluent averaged 3.5 ppm for the same two days that the influent was analyzed, however. This indicates that there is probably little if any change in phenols in the lagoon. The sampling schedule does not permit proper evaluation of detention time. The wide variation (3.0 - 27.5 ppm) in phenol concentrations in the lagoon effluent indicates considerable variation in the phenol content of the wastes. It would be necessary to obtain more phenol data before drawing any definite conclusions, however.

The average daily quantities and removals of waste constituents in the lagoon are as follows:

Quantities of Waste Constituents

	Influent	Effluent	Removal	Per Cent Removal
Weighted threshold odor				
Cold	5,260	1,720	3,540	67
Hot	6,430	1,580	4,850	75
Oxygen consumed ($K_2Cr_2O_7$), lb/day	71,400	48,800	22,600	32
5-day B.O.D., lb/day	33,300	27,000	6,300	19
Phenols, lb/day	82	310	-228(1)	-280(1)
Oils, lb/day	5,330	1,090	4,240	80

(1) Indicates increase, rather than decrease. If only data for June 9 & 11, 1953 are considered, then quantities of phenols in influent and effluent are equal (82 lbs/day).

The average flow of wastes through the lagoon during the period of the survey was 2.92 MGD.

It is difficult to say what types of phenols are present, but qualitative laboratory results indicated they are not tertiary butyl catechol.

D. Total Treatment Efficiency - The average, over-all efficiency of the treatment units in removing waste constituents from the contaminated wastes is as follows:

	Quantities of Waste Constituents			
	Charged to Treatment	Lagoon Effluent	Removed	Per Cent Removal
Weighted threshold odor				
Cold	84,200	1,720	82,480	98
Hot	104,000	1,580	102,480	99
Oxygen consumed ($K_2Cr_2O_7$), lb/day	115,000	48,800	66,200	58
5-day B.O.D., lb/day	52,200	27,000	25,200	48

14. Total Wastes Discharged from Plant

The total volumes and net quantities of waste constituents discharged from the plant, during the period of the survey, are as follows:

		Net Quantities					
Source	Volumes MGD	Weighted Threshold Odor Cold	Weighted Threshold Odor Hot	Oxygen Consumed $K_2Cr_2O_7$ lb/day	5-Day B.O.D. lb/day	Phenols lb/day	Oils lb/day
Main Outfall	127						
Gross		21,600	12,300	32,400	6,540	100	7,180
Net		20,000	10,800	7,400	4,460	0	1,360
Lagoon effluent	2.92						
Gross		1,770	1,580	48,800	27,000	310	1,090
Net		1,680	1,550	48,200	27,000	310	960
30" line to Raccoon Creek	8.4						
Gross		170	120	570	320		
Net		150	44	0	260		
Phthalic anhydride plant	3.01						
Gross		48	69	910	330		
Net		30	33	580	240		
Total Gross	141	23,500	14,100	82,700	34,200	410	8,270
Total Net		21,900	12,400	56,200	32,000	310	2,320

The population equivalent (based on net B.O.D.) for the plant is 192,000.

The percentages of total volumes and total net quantities of waste constituents, contributed by each outfall, are as follows:

Outfall	Volume	Weighted Threshold Odor		Oxygen Consumed ($K_2Cr_2O_7$)	5-Day B.O.D.
		Cold	Hot		
	Per	Cent			
Main outfall	90	91.4	87.0	13.2	14.0
Lagoon effluent	2	7.8	12.4	85.8	84.5
30" line to Racoon Creek	6	.7	.3	0	.8
Phthalic anhydride	2	.1	.3	1.0	.7
Total	100	100	100	100	100

15. Over-All Treatment Efficiency (based on butadiene and styrene operations)- The over-all efficiency of the facilities for removing waste constituents from the butadiene and styrene process wastes is as follows:

	Quantities of Waste constituents - lbs.				Per Cent Removal
	Discharged from Butadiene and Styrene Operations			Removed	
	Main Outfall	Charged to Treatment	Total		
Weighted threshold odor					
Cold	21,600	84,200	105,800	82,480	78
Hot	12,300	104,000	116,300	102,480	88
Oxygen consumed ($K_2Cr_2O_7$)	32,400	115,000	147,400	66,200	45
5-day B.O.D.	6,540	52,200	58,740	25,200	43

TABLE C-1 SUMMARY OF DAILY ANALYSES

CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS
WASTE LINES AND TREATMENT

Chemical Division
Koppers Company
Kobuta, Pennsylvania

Date 1952	Flow MGD	Threshold Odor Number		pO		Weighted Odor (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-Day B.O.D.		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	
BENZENE PLANT AREA MANHOLE No. 41 - SAMPLING POINT NO. 41 (1) 8 hour composite (increment each hour)												
June 2	1.22	32	16	5	4	39.0	19.5	12.5	127	2.44	24.8	6.7
June 3	0.43	2560000	1280000	21.3	20.3	1100000	550000	6800	24360	2160	7740	7.0
Average	0.82	-	-	13	12	-	-	-	-	-	-	-
BUTADIENE WASTE STILL CONDENSER WATER UNNUMBERED MANHOLE, SAMPLING POINT NO. X 8 hour composite (increment each hour)												
June 4	4.87	4	8	2	3	19.5	39.0	2.4	97.4	1.80	73.0	6.8
June 5	4.87	16	32	4	5	77.9	1558	6.4	260.0	-	-	6.7
Grab Sample												
June 20	4.87	-	-	-	-	-	-	-	-	0.68	27.6	-
Average	4.87	8	16	3	4	39	78	4.4	179	1.2	50	-

(1) Note: The inlet and outlet to manhole number 41 were submerged and a considerable amount of oil-like material was observed floating on the water during the period of sampling. Samples from manhole number 41 are not considered to be representative of the waste flowing in the sewer.

TABLE C-1 SUMMARY OF DAILY ANALYSES Cont'd - 2

CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS
WASTE LINES AND TREATMENT

Chemical Division
Koppers Company
Kobuta, Pennsylvania

Date 1952	Flow MGD	Threshold Odor Number		pO		Weighted Odor (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-Day B.O.D.		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	
ALTERNATE LINE AT POWER HOUSE FOR ASH SLUICING WASTES-MANHOLE NO. 45, SAMPLING POINT No. 45 8 hour composite (increment each hour)												
June 4	Negligible	4	8	2	3	-	-	111.0	-	68.0	-	7.8
June 5	Negligible	32	64	5	6	-	-	59.6	-	30.3	-	7.9
Average		11	23	3.5	4.5	-	-	85	-	49	-	-
STORAGE AND MAINTENANCE AREA, MANHOLE NO. 19, SAMPLING POINT NO. H2 4 hour composite June 2, 8 hour composite June 3 (increment each hour)												
June 2	Negligible	1600	800	10.6	9.6	-	-	170	-	51	-	7.4
June 3	Negligible	3200	6400	11.6	12.6	-	-	4860	-	305	-	7.2
Average		2020	2020	11.1	11.1	-	-	2520	-	180	-	-
OIL SKIMMER EFFLUENT - SAMPLING POINT NO. 10 8 hour composite (increment each hour)												
June 9	1.190	102400	51200	16.6	15.6	121900	60900	9290	92100	5500	54500	4.5
June 10	1.159	10000	10000	13.3	13.3	11600	11600	7590	73300	4940	47700	4.6
June 11	1.196	16000	32000	14.0	15.0	19100	38300	6840	68100	4040	40200	4.4
June 12	1.239	8000	16000	13.0	14.0	9900	19800	7850	81000	4880	50400	4.4
Average	1.20	18700	23000	14.2	14.5	22400	27600	7890	78600	4840	48200	4.4-4.6

TABLE C-1 SUMMARY OF DAILY ANALYSES Cont'd - 3

CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS
WASTE LINES AND TREATMENT

Chemical Division
Koppers Company
Kobuta, Pennsylvania

Date	Flow	Threshold Odor Number		pO		Weighted Odor (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-Day B.O.D.		
1952	MGD	Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	pH
		OIL CRACKING AND POLYSTYRENE WASTES TO RACOON CREEK - SAMPLING POINT NO. V 8 hour composite (increment each hour)										
June 4	8.40	25	12.5	4.6	3.6	210	105	3.1	217	6.05	423	6.4
June 5	8.40	16	16.0	4	4	134	134	13.2	924	-		6.9
						Grab Sample						
June 20	8.40	-	-	-	-	-	-	-	-	2.96	207	-
Average	8.40	20	14	4.3	3.8	170	120	8	570	4.5	320	-
		PHTHALIC ANHYDRIDE PLANT OUTFALL, SAMPLING POINT NO. W4 8 hour composite (three increments)										
June 16	3.01	32	32	5	5	96.3	96.3	36.6	918	16.9	424	6.3
June 17	3.01	8	16	3	4	24.1	48.2	36.1	905	9.4	236	6.4
Average	3.01	16	23	4	4.5	48	69	36	910	13	330	-

TABLE C-1 - SUMMARY OF DAILY ANALYSES Cont'd - 4

Chemical Division
Koppers Company, Inc.
Kobuta, Pennsylvania

CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS-WASTE LINES AND TREATMENT

Date 1952	Flow MGD	Threshold Odor Number		$pO^{(1)}$		Weighted Odor (Threshold)(2)		Oxygen Consumed $K_2Cr_2O_7$		5-Day B.O.D.		Phenols		Oils		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	ppm	lb/day	ppm	lb/day	
RAW RIVER WATER - PUMPING STATION INTAKE, SAMPLING POINT NO. 1 24 Hour Composite (Increment each hour)																
May 14-15	132.9	18	-	4.2	-	2392	-	56.1	62,000	2.14	2,370	-		-		6.6
May 15-16	133.6	40	-	5.3	-	5344	-	72	80,200	1.43	1,590	-		-		6.3
May 18-19	138.2	80	-	6.3	-	11056	-	52	60,000	4.53	5,220	-		-		6.6
May 19-20	136.4	80	-	6.3	-	10912	-	27.7	31,500	3.73	4,240	-		5.3	6030	6.6
May 20-21	140.4	80	-	6.3	-	11232	-	23.4	27,400	3.17	3,710	-		12.4	14500	6.4
May 21-22	138.7	10	-	3.3	-	1387	-	53.7	62,000	2.79	3,220	-		-		7.2
24 hour composite (Increment every 4-hr. from continuous sample)																
May 25-26	132.5	10	-	3.3	-	1325	-	22.5	24,800	1.69	1,870	-		-		6.7
May 26-27	132.8	20	8	4.3	3.0	2656	1062	41.1	45,500	1.70	1,880	-		-		6.5
May 27-28	133.9	20	10	4.3	3.3	2678	1339	32.2	35,900	1.30	1,450	0.080	89	-		6.5
May 28-29	136.8	2	2	1.0	1.0	274	274	22	25,100	1.18	1,350	-		-		6.7
June 2-3	133.9	16	8	4.0	3.0	2142	1071	1.8	2,010	0.92	1,030	-		3.2	3580	6.9
June 3-4	137.1	32	32	5.0	5.0	4387	4387	4	4,570	0.60	686	0.100	110	-		7.0
June 4-5	134.5	2	2	1.0	1.0	269	269	14.1	15,800	0.80	900	0.100	110	3.2	3590	7.2
June 5-6	134.6	2	16	1.0	4.0	269	2154	12.8	14,400	0.88	990	-		-		7.0
June 9-10	150.6	4	8	2.0	3.0	602	1204	7.5	9,430	1.01	1270	-		-		6.9
June 10-11	147.2	4	8	2.0	3.0	588	1178	6.9	8,480	1.40	1720	-		-		6.7
June 11-12	147.9	16	64	4.0	6.0	2366	9466	14.2	17,500	3.52	4340	-		-		6.5
June 12-13	131.0	4	16	2.0	4.0	524	2096	4.4	4,820	1.52	1660	-		-		6.7
June 16-17	151.8	4	8	2.0	3.0	607	1214	11.9	15,100	2.54	3220	-		-		6.3
June 17-18	154.7	8	16	3.0	4.0	1238	2476	14.2	18,300	4.62	5960	-		3.6	4650	6.2
June 18-19	156.9	64	128	6.0	7.0	10042	20084	9.3	12,200	1.08	1410	0.100	130	-		6.7
June 19-20	144.9	32	16	5.0	4.0	4637	2318	15.2	18,400	0.71	860	-		-		6.7
Average	140	13	12	3.70	3.62	1820	1680	23.6	27,055	1.97	2316	0.10	110	5.5	6470	

(1) pO is a mathematical expression for odor concentration. It is the number of successive dilutions (in the geometric progression where $ = 1/2) required to reach the odor concentration. See 8th edition of Standard Methods for the Examination of Water & Sewage, 1936. These values were obtained from the threshold odor number values and consequently are not whole numbers.

(2) Weighted threshold odor = threshold odor number X flow in millions of gallons.

TABLE C-1 - SUMMARY OF DAILY ANALYSES Cont'd - 5

CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS-WASTE LINES AND TREATMENT

Date 1952	Flow MGD	Threshold Odor Number		pO		Weighted Odor (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-Day B.O.D.		Phenols		Oils		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	ppm	lb/day	ppm	lbs/day	
MAIN PLANT OUTFALL - SAMPLING POINT NO. 2 24 hour composite (Increment each hour)																
May 14-15	119.3	800	-	9.6	-	95,440	-	104.6	103,950	3.05	3031	-	-	-	-	7.3
May 15-16	120.0	1600	-	10.6	-	192,000	-	44.0	43,940	2.56	2558	-	-	-	-	6.5
May 18-19	124.6	1600	-	10.6	-	199,360	-	25.8	26,780	9.32	9673	-	-	-	-	6.4
May 19-20	122.8	800	-	9.6	-	98,240	-	33.0	33,760	11.48	11740	-	-	11.8	12,070	6.9
24 Hour Composite (Increment every 4 hours from continuous sample)																
May 20-21	126.9	800	-	9.6	-	101,520	-	36.5	38,580	8.04	8498	-	-	8.7	9,196	5.1
May 21-22	125.4	1600	-	10.6	-	200,640	-	47.0	49,070	8.72	9104	-	-	-	-	6.6
May 25-26	119.2	400	-	8.6	-	47,680	-	33.3	33,060	6.80	6752	-	-	-	-	6.6
May 26-27	119.5	200	64	7.6	6.0	23,900	7658	35.8	35,640	4.72	4698	-	-	-	-	6.7
May 27-28	120.5	50	100	5.6	6.6	6,025	12050	18.2	18,270	3.56	3570	0.060	60.2	-	-	6.7
May 28-29	123.1	25	50	4.6	5.6	3,078	6160	52.9	54,240	3.80	3896	-	-	-	-	7.0
Jun 2-3	120.4	200	800	7.6	9.6	24,080	96320	10.7	10,730	5.92	5937	-	-	4.2	4,212	6.7
Jun 3-4	123.6	50	100	5.6	6.6	6,180	12360	16.6	17,091	4.60	4736	0.100	103.0	-	-	7.3
Jun 4-5	121.0	50	100	5.6	6.6	6,050	12100	17.5	17,640	5.16	5201	0.100	100.8	3.1	3,124	6.7
Jun 5-6	121.2	200	100	7.6	6.6	24,220	12120	27.0	27,260	4.96	5008	-	-	-	-	6.7
Jun 9-10	137.2	100	100	6.6	6.6	13,720	13720	16.1	18,400	5.52	6309	-	-	-	-	6.5
Jun 10-11	133.9	50	50	5.6	5.6	6,695	6695	21.5	23,980	6.96	7763	-	-	-	-	6.9
Jun 11-12	134.6	100	50	6.6	5.6	13,460	6730	17.8	19,960	4.68	5247	-	-	-	-	6.8
Jun 12-13	117.5	100	50	6.6	5.6	11,750	5875	24.8	24,270	6.80	6656	-	-	-	-	6.5
24 hour composite (Increment every hour 8:00 AM to 4:00 PM; quadruple increment every 4 hours 4:00 PM to 8:00 AM)																
Jun 16-17	138.2	32	64	5.0	6.0	4,422	8845	21.4	24,640	3.32	3822	-	-	-	-	6.5
Jun 17-18	141.2	100	200	6.6	7.6	14,120	28240	22.9	26,940	11.32	13310	-	-	6.2	7,290	6.2
Jun 18-19	143.5	50	100	5.6	6.6	7,175	14350	23.4	27,970	5.20	6215	0.120	143.4	-	-	6.7
Jun 19-20	131.4	100	200	6.6	7.6	13,140	26280	32.4	35,460	9.20	10070	-	-	-	-	6.4
Average	127	170	97	7.4	6.6	21,600	12300	31.0	32,400	6.17	6540	0.095	101.8	6.8	7,180	6.6

Chemical Division
Koppers Company, Inc.
Kobuta, Pennsylvania

TABLE O-1 - SUMMARY OF DAILY ANALYSES Cont'd - 6

CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS-WASTE LINES AND TREATMENT

Date 1952	Flow MGD	Threshold Odor Number		pO		Weighted Odor (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-Day B.O.D.		Phenols		Oils		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	ppm	lb/day	ppm	lbs/day	
LAGOON EFFLUENT - SAMPLING POINT NO. 3 24 hour composite (Increment each hour)																
May 14-15	3.088	8000	-	13.0	-	24,700	-	2,097	53,940	986	25,360	-	-	-	-	6.9
May 15-16	3.015	2000	-	11.0	-	6,030	-	2,064	51,840	780	19,590	-	-	-	-	6.8
May 18-19	3.045	1250	-	10.3	-	3,806	-	2,029	51,470	1140	28,920	-	-	-	-	6.8
May 19-20	3.087	1000	-	10.0	-	3,087	-	2,044	52,560	964	24,790	-	-	44.2	1136	6.9
May 20-21	2.960	1000	-	10.0	-	2,960	-	2,009	49,540	1140	28,110	-	-	50.8	1253	6.6
May 21-22	2.773	800	-	9.6	-	2,218	-	2,039	47,100	1220	28,180	-	-	-	-	6.6
24 hour composite (Increment every 4 hours from continuous sample																
May 25-26	2.789	400	-	8.6	-	1,116	-	2,064	47,950	1182	27,460	-	-	-	-	6.8
May 26-27	2.764	200	513	7.6	9.0	553	1106	2,072	47,700	1255	28,900	-	-	-	-	6.9
May 27-28	2.860	400	400	8.6	8.6	1,140	1140	2,021	48,150	1027	24,470	15.0	357.4	-	-	6.9
May 28-29	3.129	400	400	8.6	8.6	1,252	1252	-	-	1370	35,710	-	-	-	-	6.9
June 2- 3	2.936	800	1600	9.6	10.6	2,349	4698	2,072	50,860	1187	29,000	-	-	34.0	832	7.2
June 3- 4	2.994	800	800	9.6	9.6	2,395	2395	2,102	52,420	1187	29,600	15.0	374.0	-	-	6.5
June 4- 5	2.989	1600	1600	10.6	10.6	4,782	4782	2,174	54,130	1293	32,190	12.5	311.2	38.9	969	6.6
June 5- 6	2.853	1600	800	10.6	9.6	4,565	2282	2,129	50,600	1293	30,730	-	-	-	-	6.5
June 9-10	2.885	400	400	8.6	8.6	1,154	1154	1,996	47,970	1160	27,880	3.0	72.1	-	-	6.7
June 10-11	2.712	200	400	7.6	8.6	542	1084	1,970	44,500	1253	28,310	-	-	42.3	956	7.0
Jun 11-12	2.791	200	200	7.6	7.6	558	558	1,933	44,940	1163	27,040	4.0	93.0	-	-	7.0
Jun 12-13	2.904	400	400	8.6	8.6	1,162	1162	1,859	44,970	1130	27,340	-	-	69.5	1681	6.7
Jun 16-17	3.050	200	200	7.6	7.6	610	610	1,865	47,380	860	21,850	-	-	-	-	6.8
Jun 17-18	2.922	400	800	8.6	9.6	1,169	2338	1,799	43,790	763	18,570	-	-	33.5	815	6.8
Jun 18-19	2.870	400	1600	8.6	10.6	1,148	4592	1,857	44,400	1030	24,620	27.5	657.4	-	-	7.0
Jun 19-20	2.862	200	400	7.6	8.6	572	1145	-	-	1067	25,440	-	-	-	-	7.0
Average	2.92	590	540	9.20	9.09	1,720	1580	2,010	48,800	1110	27,000	12.8	311	44.7	1090	-

TABLE C-1 - SUMMARY OF DAILY ANALYSES Cont'd - 7

CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS-WASTE LINES AND TREATMENT

Date 1952	Flow MGD	Threshold Odor Number		pO		Weighted Odor (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-Day B.O.D.		Phenols		Oils		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	ppm	lb/day	ppm	lbs/day	
LAGOON INFLUENT - SAMPLING POINT NO. 4																
24 hour composite (increment every 4 hours from continuous sample)																
May 14-15	3.088	2000	-	11	-	6176	-	2761	71,000	1159	29,800	-	-	-	-	7.4
May 15-16	3.015	2000	-	11	-	6030	-	2664	66,900	1108	27,830	-	-	-	-	9.7
May 18-19	3.045	4000	-	12	-	12180	-	3116	79,000	1625	41,220	-	-	-	-	9.7
May 19-20	3.087	1000	-	10	-	3087	-	3185	81,940	1238	31,840	-	-	-	-	11.3
May 25-26	2.789	3200	-	11.6	-	8920	-	3904	90,700	1650	38,330	-	-	-	-	6.2
May 26-27	2.764	3200	-	11.6	-	8840	-	3748	86,290	1820	41,900	-	-	-	-	10.6
May 27-28	2.860	3200	1600	11.6	10.6	9150	4580	3364	80,140	1363	32,470	-	-	-	-	7.5
8 hour composite (increment every 4 hours from continuous sample)											(1)					
May 28	3.129	800	1600	9.6	10.6	2500	5000	-	-	1560	40,660	-	-	-	-	10.1
June 9	2.885	800	800	9.6	9.6	2310	2310	2307	55,440	1270	30,520	2.00	48.1	-	-	10.6
June 10	2.712	800	1600	9.6	10.6	2170	4340	2269	51,260	1240	28,010	-	-	153.7	3470	10.6
June 11	2.791	800	6400	9.6	12.6	2230	17860	2753	64,000	1240	28,830	5.00	116.2	-	-	9.8
June 12	2.904	6400	6400	12.6	12.6	18580	18580	2423	58,610	1177	28,470	-	-	297.2	7190	9.5
Average	2.92	1800	2200	10.8	11.1	5260	6430	2950	71,400	1370	33,300	3.5	82.1	225	5330	-

(1) 8:00 AM - 4:00 PM

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TABLE C-1 - SUMMARY OF DAILY ANALYSES Cont'd - 8

CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS - WASTE LINES AND TREATMENT

Date 1952	Flow MGD	Threshold Odor Number Cold		pO Cold	Hot	Weighted Odor (Threshold) Cold		O_2 Consumed $K_2Cr_2O_7$ ppm		5-Day B.O.D. ppm		Phenols ppm		Oils ppm		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	ppm	lb/day	ppm	lbs/day	
TOTAL OIL SKIMMER INFLUENT - SAMPLING POINT NO. 5 24 hr. composite (Increment each hour)																
May 14-15	1.532	8000	-	13	-	12,256	-	6350	81,036	2820	35,988					3.5
May 15-16	1.522	$1x10^{12(1)}$	-	40	-	$1.5x10^{12(1)}$	-	7644	96,913	2545	32,266					3.6
May 18-19	1.546	250000	-	18	-	386,500	-	7820	100,707	2760	35,544					3.5
May 19-20	1.531	50000	-	15.6	-	76,550	-	9584	122,227	3555	45,338					4.3
May 25-26	1.463	10000	-	13.3	-	14,630	-	10175	124,000	4588	55,913					3.8
May 26-27	1.484	20000	-	14.3	-	29,680	-	10494	129,724	4729	58,458					3.9
May 27-28	1.474	256000	256,000	18	18	377.344	377.344	10286	126,296	3697	45,390					3.6
TOTAL OIL SKIMMER INFLUENT - SAMPLING POINT NO. 5 8 hr. composite (Increment each hour)																
May 28	1.571	16000	16,000	14	14	25,136	25,136	-	-	3990	52,215					3.2
Average	1.52	49300	65,000	15.6	16	75,000	98,800	8910	111,600	3590	45,100					-
NEUTRALIZED STILL INFLUENT - SAMPLING POINT NO.6 25 hr. composite (Increment each hour)																
May 14-15	1.532	40,000	-	15.3	-	61,280	-	6592	84,124	2660	33,946	-	-	-	-	9.8
May 15-16	1.522	20,000	-	14.3	-	30,440	-	5651	71,645	2455	31,125	-	-	-	-	7.2
May 18-19	1.546	4,000	-	12	-	6,184	-	7056	90,868	2935	37,785	-	-	-	-	10.4
May 19-20	1.531	16,000	-	14	-	24,496	-	8820	112,484	3280	41,831	-	-	-	-	11.4
May 25-26	1.463	32,000	-	15	-	46,816	-	9735	118,638	3585	43,690	-	-	-	-	6.1
May 26-27	1.484	16,000	-	14	-	23,744	-	9281	114,729	4342	53,675	-	-	-	-	7.7
May 27-28	1.474	32,000	16,000	15	14	47,168	23,584	8223	100,966	3480	42,729	-	-	-	-	9.5
May 28-29	1.571	4,000	8,000	12	13	6,284	12,568	-	-	3420	44,756	-	-	-	-	11.2
8 hr. composite (Increment each hour)																
June 9	1.190	64,000	32,000	16	15	76,160	38,080	8431	83.573	4220	41,832	-	-	-	-	5.7
June 10	1.159	16,000	32,000	14	15	18,544	37,088	9072	87,585	3990	38,521	-	-	-	-	11.4
June 11	1.196	8,000	8,000	13	13	9.568	9,568	8404	83,726	3690	36,760	-	-	-	-	9.4
June 12	1.239	32,000	16,000	15	14	39.648	19,824	9869	101.857	4190	43,244	-	-	-	-	10.6
Average	1.41	17,800	16,700	14.1	14	25,100	23,600	8280	95,500	3520	40,800	-	-	-	-	-

(1) Not included in average value.

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TABLE C-1 - SUMMARY OF DAILY ANALYSES Cont'd - 9

CONCENTRATIONS AND QUANTITIES OF WASTE CONSTITUENTS - WASTE LINES AND TREATMENT

Date 1952	Flow MGD	Threshold Odor Number		pO		Weighted Odor (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-Day B.O.D.		Phenols		Oils		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	ppm	lb/day	ppm	lbs/day	
STILL EFFLUENT - SAMPLING POINT NO. 7																
24-hr. Composite (Increment each hour)																
May 14-15	1.601	8000	-	13	-	12,800	-	5501	73,363	2080	27,740		-	-	-	10.6
May 15-16	1.590	2000	-	11	-	3,180	-	4946	65,508	1895	25,099	-	-	-	-	9.9
May 18-19	1.616	16000	-	14	-	25,856	-	6010	80,900	2425	32,644	-	-	-	-	10.4
May 19-20	1.600	2000	-	11	-	3,200	-	6579	87,685	2060	27,456	-	-	-	-	11.5
May 25-26	1.529	1600	-	10.6	-	2,446	-	8190	104,312	2770	35,280	-	-	-	-	8.5
May 26-27	1.551	1600	-	10.6	-	2,481	-	6912	89,302	2970	38,372	-	-	-	-	10.4
May 27-28	1.540	3200	1600	11.6	10.6	4,928	2464	5828	74,763	1880	24,117	-	-	-	-	10.8
May 28-29	1.642	3200	6400	11.6	12.6	5,254	10509	-	-	2490	34,058	-	-	-	-	11.2
8-hr. Composite (Increment each hour)																
June 9	1.244	5330	2667	12.4	11.4	6,631	3318	5383	55,781	2580	26,735	6.00	62.2	-	-	5.6
June 10	1.211	3200	6400	11.6	12.6	3,875	7750	6129	61,827	2250	22,697	-	-	719.0	7253	11.2
June 11	1.250	3200	3200	11.6	11.6	4,000	4000	4873	50,740	1970	20,513	10.00	104.1	-	-	8.1
June 12	1.295	3200	12800	11.6	13.6	4,144	16576	4604	60,452	2220	23,948	-	-	9719	104842	11.0
Average	1.47	3300	4200	11.7	12.1	4,850	6180	6000	73,200	2300	28,200	8	83.2	5220	56000	-
AERATOR INFLUENT - SAMPLING POINT NO. 8																
24-hr. Composite (Increment each hour)																
May 14-15	1.487	16000	-	14.0	-	23,790	-	885	10,960	236	2,920	-	-	-	-	6.6
May 15-16	1.425	64000	-	16.0	-	91,200	-	723	8,580	406	4,820	-	-	-	-	6.7
May 18-19	1.429	32000	-	15.0	-	45,730	-	790	9,400	230	2,740	-	-	-	-	7.2
May 19-20	1.487	4000	-	12.0	-	5,950	-	428	5,300	225	2,790	-	-	-	-	6.7
May 25-26	1.260	16000	-	14.0	-	20,160	-	447	4,690	298	3,130	-	-	-	-	4.3
May 26-27	1.213	16000	-	14.0	-	19,410	-	884	8,930	660	6,670	-	-	-	-	3.7
May 27-28	1.320	4000	4000	12.0	12.0	5,280	5280	564	6,200	306	3,360	-	-	-	-	4.2
May 28-29	1.487	3200	3200	11.6	11.6	4,760	4760	595	7,730	268	3,320	-	-	-	-	7.3

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TABLE C-1 - SUMMARY OF DAILY ANALYSES Cont'd - 10

CONCENTRATION AND QUANTITIES OF WASTE CONSTITUENTS - WASTE LINES AND TREATMENT

Date 1952	Flow MGD	Threshold Odor Number		pO		Weighted Odor (Threshold)		O_2 Consumed $K_2Cr_2O_7$		5-Day B.O.D.		Phenols		Oils		pH
		Cold	Hot	Cold	Hot	Cold	Hot	ppm	lb/day	ppm	lb/day	ppm	lb/day	ppm	lbs/day	
AERATOR INFLUENT - SAMPLING POINT No.8 (Cont'd) 8 hr. Composite (Increment each hour)																
June 9	1.641	3,200	12,800	11.6	13.6	5,250	21,000	435	5,950	319	4,360	-	-	-	-	4.9
June 10	1.571	1,600	3,200	10.6	11.6	2,510	5,020	378	4,950	298	3,900	-	-	-	-	7.2
June 11	1.541	800	3,200	9.6	11.6	1,230	4,930	343	4,400	285	3,660	-	-	-	-	6.9
June 12	1.609	1,600	1,600	10.6	10.6	2,570	2,570	302	4,050	257	3,440	-	-	-	-	7.4
Average	1.46	6,300	3,600	12.6	11.8	9,200	5,260	564	6,730	316	3,760	-	-	-	-	-
Recirculation	1.524	5,500	3,800	12.4	11.9	8,400	5,800	535	6,698	282	3,579					
No "	1.32	7,700	3,600	12.9	11.8	10,200	4,750	622	6,797	383	4,120					
AERATOR EFFLUENT - SAMPLING POINT NO. 9 24 hr. Composite (Increment each hour)																
Recirculation system operating:																
May 14-15	1.487	16,000	-	14.0	-	23,790	-	389	4,820	154	1,908	-	-	-	-	6.0
May 15-16	1.425	4,000	-	12.0	-	5,700	-	294	3,490	112	1,329	-	-	-	-	7.0
May 18-19	1.429	4,000	-	12.0	-	5,716	-	98	1,166	33	393	-	-	-	-	7.1
May 19-20	1.487	1,000	-	10.0	-	1,487	-	112	1,390	30	372	-	-	-	-	7.1
Recirculation system not operating:																
May 25-26	1.260	200	-	7.6	-	252	-	106	1,112	38	399	-	-	-	-	4.3
May 26-27	1.213	1,600	-	10.6	-	1941	-	161	1,627	39	394	-	-	-	-	3.8
May 27-28	1.320	200	400	7.6	8.6	264	528	135	1,484	30	330	-	-	-	-	3.9
May 28-29	1.487	267	267	8.0	8.0	397	397	200	2,477	43	533	-	-	-	-	7.9
Recirculation system operating:																
June 9	1.641	200	200	7.6	7.6	328	328	142	1,941	75	1,025	2.00	27.3	-	-	6.5
June 10	1.571	400	200	8.6	7.6	628	314	227	2,970	128	1,675	-	-	11.1	145.3	6.8
June 11	1.541	100	200	6.6	7.6	154	308	117	1,502	74	950	3.00	38.5	-	-	6.6
June 12	1.609	200	200	7.6	7.6	322	322	97	1,300	71	952	-	-	4.1	55.0	7.3
Average	1.46	670	240	9.4	7.8	980	350	173	2,110	68.9	855	2.5	32.9	7.6	100	-
Recirculation	1.524	890	190	9.8	7.6	1,360	290	184	2,322	84	1,075					
No "	1.32	360	330	8.5	4.3	480	440	150	1,675	37	414					

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BIBLIOGRAPHY

(1) American Public Health Association, "Standard Methods for the Examination of Water and Sewage," 9th Edition, 1946.

FINAL APPENDIX

Explanation of Laboratory Analyses
and
Special Procedures for Analyses

I. EXPLANATION OF LABORATORY ANALYSES

A brief discussion of the significance of the various laboratory determinations is given below, for the purpose of aiding in the interpretation of the analytical results reported.

1. Odor

Objectionable tastes and odors in drinking water are of considerable concern to consumers, water works operators, and public health officials.(1) The control of these tastes and odors is a major problem in the field of water purification. It is believed that most tastes and odors in water supplies are due to the presence of organic chemicals. The organic impurities may arise from industrial wastes, domestic sewage, natural runoff, and the growth and decay of aquatic plants and animals.

The determination of odors and tastes in water usually makesuse of the senses of smell and taste as measuring devices of what are essentially chemical or physicochemical properties of water too small in magnitude to be detected by ordinary analytical procedures. Most tastes are represented by odors. There is a tendency to ascribe a "taste" to materials as they pass through the mouth, when the true physiological response is one of "smell" reaching the olfactory organs through the passages connecting nose and mouth.

The quality of an odor is usually designated by reference to the object from which it emanates. Our reaction to odors, furthermore, is colored by our theories of their origin. Our subjective view of odors makes their classification difficult and unsatisfactory. Since olfaction is essentially a chemical process, we should look to chemical synthesis to provide us with a more scientific means of classification of odors. There are, however, numerous difficulties to the path of satisfactory chemical classification.

The smallest amount of an odorous substance required to stimulate the olfactory nerves and obtain a concept of the odor is called the threshold value of the odor. Proceeding from threshold concentrations of odors to high intensities, we find that the increase in odor concentration necessary to cause a just perceptible increase in odor sensation, that is a threshold difference, is, within physiological limits, a definite fractional increment of the acting concentration or stimulus. If it is assumed that just perceptible differences in sensation are equal amounts of sensation, it follows that, for sensation to increase by equal amounts, that is by arithmetic progression, the stimulus must be varied by a constant fractional increment, that is by geometric progression. It is doubtful whether we should attempt to measure and express, in routine water analysis, threshold differences less than 100 per cent, or odor concentrations differing by less than 2 to 1.(2)

According to "Standard Methods," (3) the odor concentration is determined by the water dilution method. The measure of odor intensity is made by adding known amounts of odor-free water to the sample until the odor is just detectable. The reciprocal of the ratio of the volume of the undiluted to the diluted sample is called the threshold odor number. A dilution ratio of 2:1 should be used, in order to conform to the proven physiological Weber-Fechner law. When this is done, a scale of odor threshold intensities may be developed, based upon the binary geometric progression, 1, 2, 4, 8, 16, etc. This odor scale is designated by the symbol "pO," with pO being the logarithm to the base 2 of the odor threshold intensity.

Cold odor is determined at approximately 20°C, and hot odor at approximately 65°C. The vapor pressure of any compound increases with temperature, and consequently hot odor results are usually higher than cold ones.

Average threshold odor number results are arithmetic means, while average pO results are logarithmic means. Extreme values do not affect logarithmic means as much as arithmetic means.

2. Dichromate Reflux Method for Determination of Oxygen Consumed

The oxygen consumed from dichromate determination is an approximate measure of the oxygen-absorbing power of a waste. It is a wet combustion method. The measured consumption of chemical oxidant under standardized conditions indicates the amount of oxidizable organic and/or inorganic matter present in a sample. The results are expressed in parts per million oxygen. Although the method has definite limitations, it is of value in estimating the strength of industrial wastes.(4) Certain organic compounds are oxidized very slightly, while others are readily attacked. When 50 per cent by volume sulfuric acid is used in the reflux mixture, chlorides are quantitatively oxidized. The oxygen consumed values of wastes containing high chloride concentrations, therefore, can be corrected for their known chloride content.

The dichromate reflux method for determination of oxygen consumed, and the B.O.D. test, are two distinctly different parameters, indicating chemical and biological oxygen requirements. However, where a given industrial waste is fairly constant in composition and contains no toxic materials, a satisfactory O.C./B.O.D. ratio may be determined.(5) In such case, the oxygen consumed test, with occasional checks against B.O.D., may be used for control purposes. There would be a considerable saving of time.

Many wastes contain material toxic to the microflora and fauna responsible for biochemical action. The chemical oxygen consumed method can be used advantageously under such conditions, to estimate the strengths of the wastes.

3. Biochemical Oxygen Demand (B.O.D.)

The biochemical oxygen demand of sewage, polluted waters, or industrial wastes, is the oxygen (in ppm) required during stabilization of the decomposable organic matter by aerobic bacterial action. The rate of oxygen demand is dependent on both time and temperature, and consequently the standard conditions of 5 days' incubation at 20°C are usually used for the test. Approximately 68 per cent of the oxygen demand of the carbonaceous material present in normal domestic sewage is satisfied under the conditions of 5 days' incubation at 20°C. The oxygen demand rates of industrial wastes, however, may or may not follow the typical oxidation curve for domestic sewage. It would be necessary to incubate a particular sample of waste for such a period of time that no more oxygen demand was exerted, in order to determine the total B.O.D.

High B.O.D. values are objectionable from a stream pollution standpoint because they reduce the oxygen resources of the streams, adversely affecting the aquatic life. If the oxygen content is depleted, anaerobic conditions develop and the water is rendered undesirable for supply and recreational purposes.

4. pH

The symbol "pH" denotes the negative logarithm of the hydrogen-ion normality. The pH value indicates the relative acidity or alkalinity of a solution, being lower with higher degrees of acidity.

pH data are helpful in measuring the effects of acid and alkaline wastes on natural surface waters. Acids causing pH values below 4.0 and alkalies causing pH values above 10.0 are undesirable and hazardous for fish life in waters which are not naturally so acid or alkaline. pH is also an important factor when considering treatment for domestic and industrial water supplies.

5. Phenols

The phenol results, as reported, represent the gross quantity of phenolic constituents such as phenols, cresols, etc. These substances are found in variable proportions and amounts in certain types of industrial wastes. They may result, as in by-product coke and gas plant wastes, from the pyrolysis of coal.

Phenols may cause tastes and odors in water supplies. Concentrations of as little as 0.002 to 0.005 ppm phenols may produce chlorophenol (medicinal) tastes and odors in the presence of chlorine in water. A concentration of 0.1 ppm of phenol alone will impart the characteristic taste and odor of phenol to water. Phenol compounds are toxic to aquatic life, with lethal limits being dependent on such factors as concentration, time of exposure, and the characteristics of the water. The minimum concentration of phenol reported as being toxic to fish is 0.4 ppm. Fish exposed to phenolic compounds in water will acquire the tastes and odors of these compounds.

6. Oils

The oil results were obtained by extracting the samples with a 1:1 mixture (by volume) of diethyl ether and carbon tetrachloride. These results represent all of the materials which are soluble in these organic solvents, and not just the true oils as such.

Oily materials are objectionable from the standpoint of stream pollution because they are unsightly, damaging to wildlife and aquatic life, detrimental to recreational facilities, and interfere with treatment processes for public and industrial water supplies. Oily films on the surfaces of lakes and streams interfere with the normal reaeration of the water and may be difficult to remove. Certain sludges may contain oily materials which may be toxic to bottom fauna and flora.

II. SPECIAL PROCEDURES FOR ANALYSES

1. Dichromate Reflux Method for Determination of Oxygen Consumed

This procedure is described in two articles of the American Chemical Society publication, "Analytical Chemistry:"

(1) Moore, W. A., Kroner, R. C., and Ruchhoft, C. C. "Dichromate Reflux Method for Determination of Oxygen Consumed." 21, 953, Aug., 1949.

(2) Moore, W. A., Ludzack, F. J., and Ruchhoft, C. C. "Determination of Oxygen Consumed Values of Organic Wastes." 23, 1297, Sept., 1951.

2. Phenols

A. Preliminary Screening Procedure

(1) To 250 ml of sample, add 2 ml of 10% $CuSO_4$ solution and bring the pH of the mixture below 4.0 by the addition of 10% phosphoric acid solution. Put the mixture in an all-glass distilling apparatus and distill over approximately 200 ml. Halt the distillation, and allow the distilling flask to cool until boiling ceases. Add 50 ml distilled water to the distilling flask and resume the distillation until a total of 250 ml plus the volume of reagents added has been distilled over.

(2) Acidify the distillate with 1 ml of 10% phosphoric acid solution and add 5 ml of 10% $CuSO_4$ solution. Transfer

the mixture to a separatory funnel containing 75 g fine-grained C.P. sodium chloride. Make three serial extractions with C.P. chloroform. On the first extraction, shake the mixture until the salt has completely dissolved. Use 50 ml of chloroform per extraction. Collect the chloroform extracts, discarding the aqueous phase after the third extraction. Combine the chloroform extracts. Extract the chloroform twice with 75 ml portions of 0.1 N sodium hydroxide. Discard the extracted chloroform. Combine the alkaline extracts and make it up to 250 ml, using a volumetric flask.

(3) Repeat item (1).

B. Estimation of Phenols

(A) Bromination Procedure - for phenol concentrations over 10 ppm.

(1) Take an aliquot portion of the NaOH extract obtained in the screening procedure (the portion so taken that it contains about 0.05 g phenol) and dilute to exactly 200 ml.

(2) Place sample in 500-ml glass-stoppered Erlenmeyer flask and add 50 ml of bromate-bromide solution (2.784 g $KBrO_3$ + 10 g KBr diluted to 1 L with distilled water), followed by 5 ml of conc. HCl.

(3) After 60 minutes, add 2 g KI.

(4) Titrate the liberated iodine with 0.1 N thiosulfate solution in the presence of starch indicator.

(5) Run a blank in the same manner as the sample.

(6) Calculation of phenol:

1 ml of 0.1 N thiosulfate = 0.001567 g phenol

$$\text{ppm phenol} = \frac{(\text{ml for blank} - \text{ml for sample})\ 1.567 \times 1000}{\text{ml of sample}}$$

(B) Gibbs Procedure - for phenol concentrations under 10 ppm.

(1) Use the method in Standard Methods, 9th ed., page 216.

Standard phenol solution may be made from C.P. phenol alone, rather than mixture of phenol and O-cresol.

3. Oils

A. Procedure

Determine the pH of the sample. If compositing is being practiced, the subsamples should be composited in a 2-liter separatory funnel and mixed before the pH is checked. If the pH is above 6.0, add 1-ml portions of 85% hydrochloric acid until the pH falls below 6. Then add a further 10-ml portion of 85% hydrochloric acid. If the pH of the sample is initially below 6.0, add 10 ml of 85% hydrochloric acid without preliminary adjustment of pH. Rinse the sample container or containers with an 80-ml portion of the extraction mixture (1:1 mixture by volume of carbon tetrachloride and diethyl ether). After the extraction mixture has been used to rinse the sample containers, transfer it to the extraction flask and shake vigorously with the sample for two minutes. The sample is allowed to stand long enough for the solvent layer to separate. The lower solvent layer is then separated. Rinse the sample container or containers with a further 60-ml portion of solvent. Add the solvent to the sample in the separatory funnel and shake for two minutes. Separate the solvent layer and add it to the solvent already collected from the first extraction. Make a third rinsing and extraction, using a further 60-ml portion and the same technique as was used for the second extraction.

Put the combined extract portions into the separatory funnel with 1 liter of distilled water and shake thoroughly for two minutes. Separate the extract and wash the distilled water with 30 ml of extraction mixture. Add the wash solvent to the separated extract. Filter the combined extract portions through a fat-free filter paper. Wash the paper three times with 5-ml portions of solvent, combining the filtrate and the wash solvent. Evaporate the combined extract on a steam bath under a hood in a weighed evaporating dish. When the solvent has been evaporated, transfer the dish to an oven maintained at 103°C. Dry for 30 minutes and cool in a desiccator. Reweigh the dish.

B. Calculation:

$$\frac{\text{Weight of oil in mg}}{\text{Volume of sample in liters}} = \text{ppm "oil"}$$

Note: With a few samples, the solvent will not separate completely from the sample, but forms a heavy solvent-in-water emulsion which will sink to the bottom of the separatory funnel. With such samples, the emulsion should be separated. When the emulsions are all collected, they may usually be broken by shaking with 500 ml of 1% hydrochloric acid in a separatory funnel. In rare cases, several washes may be required. Regardless of whether one or two rinses are required, the wash water should be given one cleanup extraction with 30 ml of solvent after the main body of the solvent has been separated. The wash solvent is separated and added to the main body of the solvent. It is then washed with water, etc.

REFERENCES

(1) Middleton, F. M., Braus, Harry, and Ruchhoft, C. C. "Fundamental Studies of Taste and Odor in Water Supplies." J. Am. W. W. Assoc., 44, 6, 538, June, 1952.

(2) Fair, G. M. "On the Determination of Odors and Tastes in Water." J. New Eng. W. W. Assoc., 47, 248, (1933).

(3) "Standard Methods for the Examination of Water and Sewage," 9th Edition, 1946, Am. Public Health Assoc.

(4) Moore, W. A., Kroner, R. C., and Ruchhoft, C. C. "Dichromate Reflux Method for Determination of Oxygen Consumed." Anal. Chemistry, 21, 953, Aug., 1949.

(5) Moore, W. A., and Ruchhoft, C. C. "Chemical Oxygen Consumed and Its Relationship to B.O.D." Sewage and Ind. Wastes, 23, 6, 705, June, 1951

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FOR ADMINISTRATIVE USE

PART II

AT

KOBUTA PLANT
CHEMICAL DIVISION

KOPPERS COMPANY, INC.

MAY 14 TO JUNE 21, 1952

A STUDY OF THE CHEMICAL AND ODOROUS CHARACTERISTICS OF LIQUID WASTES FROM THE KOBUTA, PENNSYLVANIA PLANT OF THE KOPPERS COMPANY, INC., AND CHEMICAL AND ODOR STUDIES OF WATER SUPPLIES AT MIDLAND, PENNSYLVANIA, WEIRTON, WEST VIRGINIA AND WHEELING, WEST VIRGINIA.

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PUBLIC HEALTH SERVICE
ENVIRONMENTAL HEALTH CENTER
CINCINNATI, OHIO

ABSTRACT

Organic materials in the principal wastes from the Kobuta plant of the Koppers Company were concentrated by means of the carbon filter and liquid extraction methods. Organic materials were also concentrated from raw Ohio River water at the Kobuta pumping plant and from the water supplies at Midland, Pa., Weirton, W. Va., and Wheeling, W. Va. The chemical characteristics and odor properties of these materials were studied to determine whether a relationship existed between the materials discharged by the Kobuta plant and materials believed to cause odor in the water of the above-named cities.

The neutral components of the Kobuta wastes comprised 55 to 85 per cent of the total organic material recovered. This material also had the odor most characteristic of the entire waste. Partial separation and determination of the characteristics of major odorous components was accomplished.

The organic materials recovered from the water supplies of the cities were tested for chemical and odor characteristics. The material recovered was a complex mixture that is unidentified at present. However, chemical separation, fractional distillation, and other determinations, indicated that the material was not the same as that recovered from the Kobuta wastes. Odor characteristics of the water at the cities of Midland, Weirton and Wheeling, during the survey period, could not be associated directly with odors from the Kobuta waste.

Computations of the quantities of odorous materials discharged by the Kobuta plant, river flow data, and odor characteristics of the material, indicated that odor trouble would not be expected under the conditions experienced during the study. Breaks, spills, lapses in treatment, or other occurrences that might cause unusual amounts of wastes to be discharged from Kobuta, could bring about odorous conditions in downstream water supplies.

INTRODUCTION

Tastes and odors in water supplies on the upper Ohio River have been a problem for a number of years. Water purification plants in this area have been generally successful in providing palatable water, under difficult conditions. In some instances the water may be classed as acceptable rather than palatable, inasmuch as the consumers tolerate a moderate level of taste and odor. Sporadically, tastes and odors become acute and none of the ordinary water treatment methods are effective in removing the objectionable materials.

Odorous materials in water arise from many sources. Among these, industrial wastes are noteworthy for their complexity and variety. In some instances, industrial wastes have been established as causes of taste and odor problems. These problems may arise even when the concentration of odorous substances in the water is extremely low. For these reasons, the determination of the identity and origin of such materials is a task of formidable proportions.

Among the possible sources of odorous material being discharged into the upper Ohio River are wastes from the Kobuta, Pa., plant of the Chemical Division of the Koppers Company, Inc. The principal products manufactured by this plant are butadiene and styrene. In connection with and supplementary to an industrial waste survey * of

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* See report. "A Study of the Characteristics of Liquid Wastes from a Chemical Plant Producing Ingredients for Synthetic Rubber Production," by D. M. Taylor and R. L. Harris, Jr., Public Health Service, Cincinnati, Ohio.

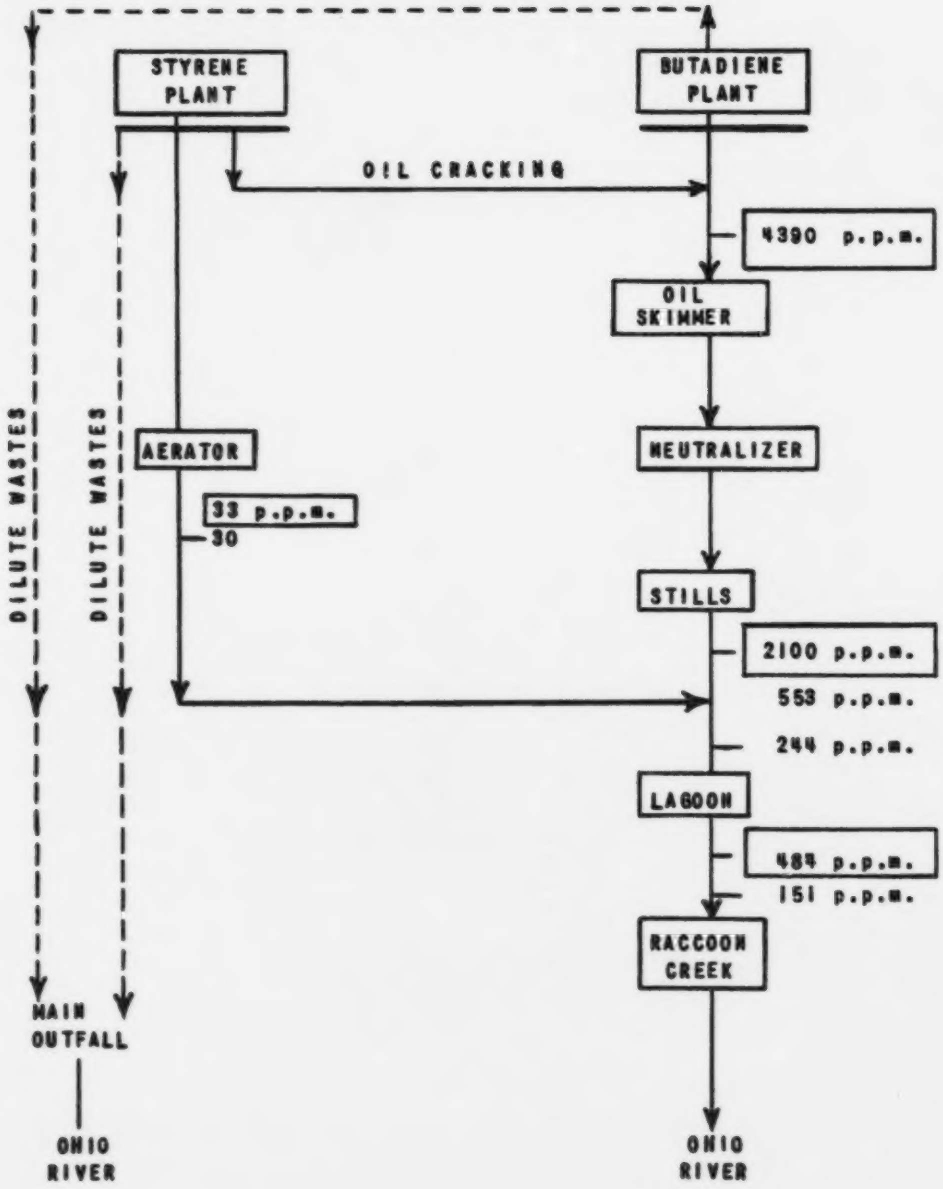
the Kobuta plant wastes, a study was made of the chemical and odorous characteristics of the Kobuta wastes and of organic materials that could be recovered from the water supplies of Midland, Pa., Weirton, W. Va., and Wheeling, W. Va. These cities are, respectively, 3 miles, 31 miles, and 56 miles, by river, below the Kobuta plant. It was the purpose of the study to determine whether materials discharged by the Kobuta plant were causing odor problems in the water supplies of these cities.

To facilitate study, the organic materials in the wastes and water supplies were concentrated by liquid-liquid extraction methods and adsorption on activated carbon filters. The application of these techniques and the results of the study of the recovered organic material constitute the subject of this report.

LIQUID EXTRACTION OF WASTES

Samples taken at six points in the Kobuta waste system were concentrated by liquid extraction methods. The waste samples were acidified to a pH of 3.0 with sulfuric acid and extracted with diethyl ether in an apparatus designed for continuous countercurrent flow. (1) The solvent was distilled and the yields of waste residues were determined.

The sampling points and yields of extract are shown in the accompanying simplified flow diagram. One set of values represent grab samples taken on April 30, 1952. The set of values appearing in boxes represent one-day composite samples collected on June 8, 1952. The values shown are indicative of the ranges of concentration that occur in these wastes. In addition, samples of the main outfall effluent and


STYRENE PLANT
BUTADIENE PLANT
OIL CRACKING
4390 p.p.m.
OIL SKIMMER
NEUTRALIZER
DILUTE WASTES
DILUTE WASTES
AERATOR
33 p.p.m.
30
STILLS
2100 p.p.m.
553 p.p.m.
244 p.p.m.
LAGOON
484 p.p.m.
151 p.p.m.
RACCOON CREEK
MAIN OUTFALL
OHIO RIVER
OHIO RIVER

FLOW DIAGRAM

KOBUTA WASTES

AT

KOPPERS CO., INC., KOBUTA, PA.

ENVIRONMENTAL HEALTH CENTER

the lagoon effluent were obtained by adsorption on activated carbon filters. Other tests have shown that recoveries from carbon filters are approximately half the yields obtained by liquid extraction of the same waste.

PROPERTIES OF ORGANIC MATERIALS RECOVERED FROM WASTE

The preponderance of organic material and the characteristic waste odor, evident even in the plant area atmosphere, occurred in the butadiene plant waste stream and the lagoon effluent. Therefore, samples at points in this stream were chosen for further chemical investigation. Because of the low organic content and low odor intensity of main outfall samples obtained during this part of the survey, this stream was not studied in detail.

The organic residues recovered by the carbon filter and liquid extraction techniques were separated into acidic, phenolic and neutral classes of compounds. Extractions under alkaline conditions indicated that organic bases were present in negligible quantities. The neutral class of compounds was present in quantities from 55 to 85 per cent of the total extract. Organic acids were also present in amounts ranging from 5 per cent to 40 per cent. The proportion of phenols was small. In each sample, the characteristic waste odor resided in the neutral fraction. It is probable that this fraction, being less reactive chemically, would survive in a stream longer than the other materials in the waste. The neutral fractions of the oil skimmer influent and lagoon effluent were selected for detailed study.

Oil Skimmer Influent

The characteristic heavy odor of the waste was intensified in the neutral fraction. The neutral materials were fractionally distilled at a pressure of 10 mm. of Hg. Five fractions and a residue were obtained. Table 1 shows the properties of these fractions. The residue was a tarry material of little odor which comprised approximately 50 per cent of the neutral group. The odors of fractions 1 and 2 were most intense, although all fractions were odorous.

Figures 2 to 6 are infrared spectrograms * of the distillate fractions described in Table 1. The spectrum of fraction 1 (Figure 2) indicates the following: A strong band at 5.9 μ indicates that the main component is a carbonyl compound, aldehyde or ketone. Since no significant bands occur at 5.75 to 5.80 μ ester is not present in more than trace amounts. Aldehyde or ketone was further demonstrated by formation of a 2, 4 - dinitrophenylhydrazone. A weak band probably caused by hydroxyl (2.9 μ) is present. In view of the relatively low molecular weight of this fraction, as indicated by the boiling range, this band would be stronger if present in the major component and probably represents a minor component. The absence of a strong band around 13.8 μ shows that the major component is not a long-chain aliphatic compound and is perhaps cyclic. From this evidence, the terpenic odor, and other tests, it is concluded that this material may be a cyclic aldehyde or ketone. Fractions 2 to 5 (Figures 3-6 show decreasing amounts of carbonyl and are suggestive of hydrocarbon materials. The odor characteristics of these fractions were also hydrocarbon-like.

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* Infrared spectra run on a Baird double beam recording spectrophotometer.

Lagoon Effluent

The organic residue recovered from the lagoon effluent by means of activated carbon resembled the organic extract of the oil skimmer influent. The neutral group was fractionally distilled as described in the section above. The odors of the lagoon effluent extract and the distillate fractions of the neutral group are indicated in Table 2. The infrared spectrum of the first distillate fraction, Figure 7, was very similar to the spectrum in Figure 2. The higher-boiling fractions also resembled the corresponding fractions obtained from the oil skimmer influent. Further separation of the odorous principles contained in the second fractional distillate of the neutral group of the lagoon effluent sample was accomplished by countercurrent distribution analysis. This analysis was carried out in an all-glass 100-tube distribution machine (2), using iso-octane and 95% ethanol as the solvent combination. Ultraviolet absorption spectra of the distributed sample indicated the presence of three components. When recovered, these components exhibited different infrared spectra and odor characteristics. The first component, containing the principal odorous material, amounted to 14% of the material used. The infrared spectrum showed strong aldehydic or ketonic carbonyl and aliphatic CH bands. Olefinic, but not aromatic, unsaturation was also revealed. This substance yielded a 2, 4-dinitrophenylhydrozone, m.p. 135-137°C. The odor of this fraction suggested terpinic material; the infrared spectrum, boiling point, and derivative melting point were all consistent with a cyclic terpena ketone structure.

A fraction constituting 72% of the sample had a kerosene-like odor. The only strong bands in the infrared spectrum were those of aliphatic hydrocarbons. Weak bands representing slight aromatic content were also present. This spectrum closely resembled the spectra of petroleum refinery wastes.

The third component could not be recovered in sufficient quantity and purity for further study. Its odor was mild.

A typical waste extract contained 20% of organic acids. In recovering the acid group a crystalline acid with acrid odor was separated, resembling crotonic acid.

EXAMINATION OF ORGANIC SUBSTANCES IN CITY WATER SUPPLIES

Carbon Filter Method

When the concentration of organic contaminants in water is very low, it is not presently practicable to perform liquid extraction on the several thousand gallons of water required to obtain sufficient extract for further study. Under such circumstances, adsorption on activated carbon was employed. The water or waste was passed slowly through the carbon contained in a long, cylindrical filter. Where clogging due to suspended matter was anticipated, a prefilter of sand and gravel was used, with facilities for backwashing. Adsorbed organic materials were extracted from the carbon by an organic solvent, which was then removed by distillation from the extract. Details of the carbon filter technique and a systematic procedure for the examination of extracts have been described by Middleton and Braus(1, 3). Recoveries by this method are not quantitative, because of losses in the filter, incomplete adsorption by the carbon, and incomplete desorption.

Properties of Organic Extracts

Carbon filters preceded by sand filters were placed on the raw water supplies at the Kobuta pumping plant, Midland, Pa., Weirton, W. Va., and Wheeling, W. Va. Figure 1 is a map of the area covered in the sampling program. The quantity of organic materials recovered from these filters is shown in Table 3. From 0.2 ppm to 0.5 ppm of organic material was the usual quantity recovered. In all instances less than 5 grams of material were recovered. This quantity of material permitted examination for the presence of Kobuta plant waste substances. The odors of the city extract materials were musty and also resembled a paint-like odor that is frequently encountered in Ohio River water extracts.

Samples of the extract obtained from Midland, Pa., and Weirton, W. Va., were separated into groups and the neutral group was fractionally distilled. These samples did not contain materials boiling in the same range as the distillate fractions of Kobuta waste in which the characteristic odor was concentrated. The first distillate fraction of the city extract neutral groups had a much higher boiling range and did not exhibit the odor characteristics of the Kobuta waste materials.

The infrared spectrogram of the first fraction of the neutral group from the Kobuta lagoon effluent extract (Figure 7) and the first fraction of the neutral group from the Weirton extract (Figure 8) are included in this report for comparison. Certain similarities exist in the two spectra, but the differences are sufficient to indicate that the two samples are not the same chemically. The absorption bands at 7.58 μ, 11.0 μ and 12.7 μ in the lagoon effluent spectrum do not appear on the Weirton spectrum. The Weirton spectrum exhibits absorption bands at 8.85, 9.7, 10.3 and 12.15 μ which are not present on the lagoon effluent spectrum. The major portion of the extracts recovered from the city filters is a high-boiling complex mixture of presently unidentified materials.

Samples of extract from the Kobuta pumping plant and Wheeling, W.Va., raw water were not examined in detail since Kobuta waste materials could not be demonstrated in Midland and Weirton samples.

ODOR MEASUREMENTS

Kobuta Wastes

Odor tests were made on certain of the organic extracts obtained from various samples by the carbon filter and liquid extraction techniques. Weighed quantities of the extracts were dissolved in odor-free water and a series of flasks containing graduated amounts of the material were tested in the usual manner to determine the threshold odor concentration. Table 2 summarizes the results of the odor determinations.

City Water Supplies

Determinations of threshold odor levels in the water supplies of the cities of Midland, Pa., Weirton, W. Va., and Wheeling, W.Va., were made during this study. Water works officials in these cities cooperated in making the tests and the trailer laboratory ran check samples. Table 4 summarizes the results of the odor tests. At Midland, the principal odors were described as musty, oily and medicinal. At Weirton, odors were described as phenolic, gassy and varnish-like. Odors in Wheeling water were described as phenolic, cresolic and muddy. No similarity between the odors in the water at the various cities and the odors in Kobuta wastes was evident during the survey.

EFFECT OF DILUTION ON ODOR PROBLEMS OF KOBUTA WASTE

The estimated discharge of the Ohio River at Kobuta during the period of the survey is shown in Table 5. Flows are expressed in cubic feet per second (cfs) and million gallons per day (MGD). From May 16 to June 1 the flow varied from 131,000 cfs to 47,800 cfs. From June 2 to June 20, the flow decreased steadily from 33,000 cfs to 8,280 cfs. Minimum flow in the Ohio River is estimated to be 2,000 cfs and the average daily flow is estimated to be 20,000 cfs.

The extent of problems caused by a waste effluent is of course directly dependent on the degree of dilution effected by the receiving stream. Accordingly, it is of interest to evaluate the effect of river dilution on Kobuta wastes. Numerous measurements of flow volumes and threshold odor numbers of the main outfall and lagoon effluent were made by the trailer laboratory. From these data, it is possible to calculate the minimum river flow required to dilute these wastes to the threshold level. These values are:

	Average Waste Flow, MGD	Geometric Mean Threshold Odor Number	Required Dilution, MGD
Main outfall	157	170	21,590
Lagoon Effluent	2.92	588	1,715
		Total	23,305

If the odor contributions of the two waste streams are considered to be additive, then the threshold odor level would be reached at river flows below 23,300 MGD. Flows were greater than this value from May 15 to June 1 and progressively below this level from June 2 to the end of the survey on June 20.

A similar computation may be based on the actual quantities of organic material discharged in the Kobuta wastes. The water as pumped from the river at the Kobuta water plant showed an average of 5.5 ppm of ether extractable (oily) materials. The main outfall of the Kobuta plant showed 6.8 ppm by similar testing. This leaves a net contribution of 1.3 ppm of organic materials in the main outfall. It may be pointed out that representative samples for the determination of oil are difficult to collect. The value of 5.5 ppm for oils on the water intake appears to be high compared to the river as a whole just above Kobuta. A series of 20 samples collected in the river above Kobuta showed an average oil content of 0.8 ppm according to the report submitted by the Pennsylvania State Health Department. The apparently high values from the water plant samples may be due to shore pollution and pulling of surface water into the intake. Using the values as found indicate the daily discharge of ether-extractable materials by Kobuta was as follows:

Main outfall 1.3 x 8.3 x 127 = 1370 lbs./day
Lagoon effluent 44.7 x 8.3 x 2.9 = 1075 lbs./day
2445 lbs./day

The total discharge is 2445 lbs./day. In the odor tests of Kobuta waste, no observer failed to detect a concentration of 0.1 ppm. Therefore, this value is taken as the concentration where an odor problem would occur. On this basis 0.83 pounds of the material will give observable odor to 1 million gallons of water. The total daily organic discharge is thus capable of causing odor contamination in the volume of river water estimated in the following calculations:

$$\frac{2445}{0.83} = 2{,}960 \text{ MGD}$$

For the period of the survey, the river flow was above this level. The effects of materials already present in the river on the odor of materials discharged by Kobuta were not ascertained on this study. The computations given here are indicative but should not be construed as absolute values.

During the twelve days from May 15 to 26, 1845 gallons of water were passed through a carbon filter at Midland, Pa., with recovery of 1.6 grams of organic extract. The total discharged organic waste material from the Kobuta plant during the same period, divided by the aggregate volume of river flow, amounted to 5.5 parts per billion, a concentration lower than the odor threshold value. The content of Kobuta waste in the water passed through the Midland filter, assuming complete mixing on the river and no losses, would be:

$$1845 \times 3.78 \times 0.005 = 38 \text{ mg. or } 0.038 \text{ grams}$$

It is therefore evident that Kobuta waste material could not comprise as much as 2.5 per cent of the organic substances in the Midland water supply. This small amount, if present, could not be demonstrated by chemical separation methods, in the absence of analytical procedures specifically applicable to Kobuta waste materials.

SUMMARY AND CONCLUSIONS

1. The wastes discharged to the Ohio River by the Koppers Company Kobuta plant are extremely complex mixtures of organic chemicals. Complete separation of the material into specific components was not feasible. Partial separation of the organic extracts was accomplished by a combination of chemical and physical methods. The principal source of odor was the neutral class of compounds. From 55 to 85 per cent of the total organic material recovered was neutral. Fractional distillation of the neutral materials yielded 50 per cent of highly odorous materials. The remainder was a relatively odorless residue.

2. Tests on organic extracts from the cities of Midland, Pa., and Weirton, W. Va., did not indicate the presence of the types of materials found in Kobuta wastes. Dilution in the river, the action of natural purification on these wastes, and the presence of organic materials from other sources, natural, domestic and industrial, probably account for this result. Odor tests at the downstream water plants did not show evidence of odors directly traceable to Kobuta effluents during the study.

3. Computations based on analyses made during the survey indicated the Kobuta plant was discharging approximately 2445 lbs. daily of ether-soluble organic materials. A concentration of 0.1 ppm (100 ppb) of the organic extract was capable of producing unmistakable odor by laboratory odor tests. The waste output of the Kobuta plant would thus produce observable odor when the river flow was less than 2960 million gallons per day. The dilution required based on threshold odors was 23,300 MGD. The persistence of these odors and other effects were not determined.

4. The wastes as discharged at Kobuta do constitute a potential odor problem in downstream water supplies. Spills, breakdowns, inadequate treatment, low river conditions, or other occurrences, may produce taste and odor in downstream water supplies. During the period of the study, treatment as practiced at Kobuta, combined with the dilution available, appeared to effectively limit possible taste and odor production. Whether the chemical and biological reactions taking place in the river on Kobuta wastes produce compounds that may affect city waters could not be ascertained and would require further research.

Table 1 - Properties of Fractional Distillates - Neutral Group - Oil Skimmer Influent

Chemical Division, Koppers Company, Kobuta, Pennsylvania

Fraction	Per Cent of Total Material	b.p. at 10 mm/Hg °C	Refractive Index 25°C	Odor
1)	15	75-90°C	1.4999	Terpene
2)		110-115	1.5158	"
3)	35	115	1.5194	Kerosene
4)		130-140	1.5235	"
5)		145-155	1.5371	"
6 (residue)	50	Residue	--	Odorless

Table 2 - Threshold Odor Concentration Results on Organic Extracts

Chemical Division, Koppers Company, Kobuta, Pennsylvania

Sample Source	Method for Recovery of Extract	Threshold Odor Concentration ppb	Type of Odor
Lagoon effluent	Carbon filter	62	Sweet-heavy
Lagoon effluent Neutral fraction	" "	62	Sweet-hydrocarbon
Lagoon effluent	Liquid extraction	80	Hydrocarbon
Lagoon effluent Neutral group	Carbon filter		
Fraction 1		16	Terpene
2		16	"
3		16	Kerosene
4		32	"
5		150	"
6		No odor	----
Weirton, W. Va. Neutral fraction	Carbon filter	256	Musty

Table 3 - Recovery of Organic Chemicals from Raw Water Supplies by Carbon Filter Technique

Chemical Division, Koppers Company, Kobuta, Pennsylvania

Date, 1952	Sample Source Raw Water	Quantity of Water Filtered gallons	Total Organics Recovered	
			grams	p.p.m.
May 15-19	Kobuta pumping plant	1010	1.88	0.49
May 28-June 11	"	5250	5.72	.29
May 15-26	Midland, Pa.	1845	1.59	.23
May 26-June 17	" "	3180	2.06	.17
June 19-July 4	" "		4.70	
May 15-25	Weirton, W. Va.	1000	2.0	.53
May 28-June 18	" "	4220	3.2	.20
May 15-27	Wheeling, W.Va.		1.6	
May 27-June 14	" "	4260	3.4	.21
June 20-23	" "	665	1.2	.48

Table 4 - Threshold Odor Results on City Raw Water Supplies

Date 1952	Midland, Pa.		Weirton, W.Va.		Wheeling, W.Va.	
	PHS	City	PHS	City	PHS	City
May 16	2			8		
17				8		
18	2			8	2	
19				8	2	
20	2			8	4	8
21				8	2	16
22	4			8	2	8
23				8		4
24				8		
25	32	7	8	8	4	8
26			2	8	4	8
27	4	10	1	8	2	4
28	2	7	1	8	2	8
29				8	4	4
30	8	10		8	8	4
31	4	7		8	8	4
June 1				8	16	4
2	64	7		8	4	4
3	2	5		8	16	4
4	2	5		8	64	8
5	4	5	32	8	16	4
6	8	5	32	8	32	8
7				8	16	8
8	16	7		4	32	8
9	16	7		4	8	16
10	8	4		4	4	16
11		5		4	4	8
12		5		4	16	16
13	8	5		4	8	8
14	8	7	16	4	16	8
15	8	7	8	4	4	4
16	8	5	8	4	2	8
17	8	5			4	8

Table 5 - Estimated Discharge, Ohio River at Kobuta, Pa., Plant, 1952

Date	Discharge	
	c.f.s.	m.g.d.
May 15	79,500	51,500
16	79,300	51,200
17	74,000	47,900
18	59,000	38,200
19	47,800	31,000
20	55,100	35,700
21	106,000	68,500
22	112,000	72,500
23	91,700	59,400
24	77,300	50,000
25	95,200	61,600
26	141,000	91,200
27	137,000	88,600
28	111,000	71,800
29	88,800	57,400
30	74,600	48,300
31	53,500	34,600
June 1	41,700	27,000
2	33,000	21,400
3	27,000	17,450
4	23,600	15,250
5	20,500	13,300
6	18,500	12,000
7	17,000	11,000
8	15,300	9,900
9	13,400	8,700
10	12,900	8,350
11	12,200	7,900
12	11,100	7,200
13	10,400	6,750
14	11,600	7,500
15	10,600	6,900
16	9,770	6,300
17	9,800	6,340
18	10,300	6,670
19	9,320	6,040
20	8,280	5,320

(Supplied by Division of Hydrography, Commonwealth of Pennsylvania)

20-a

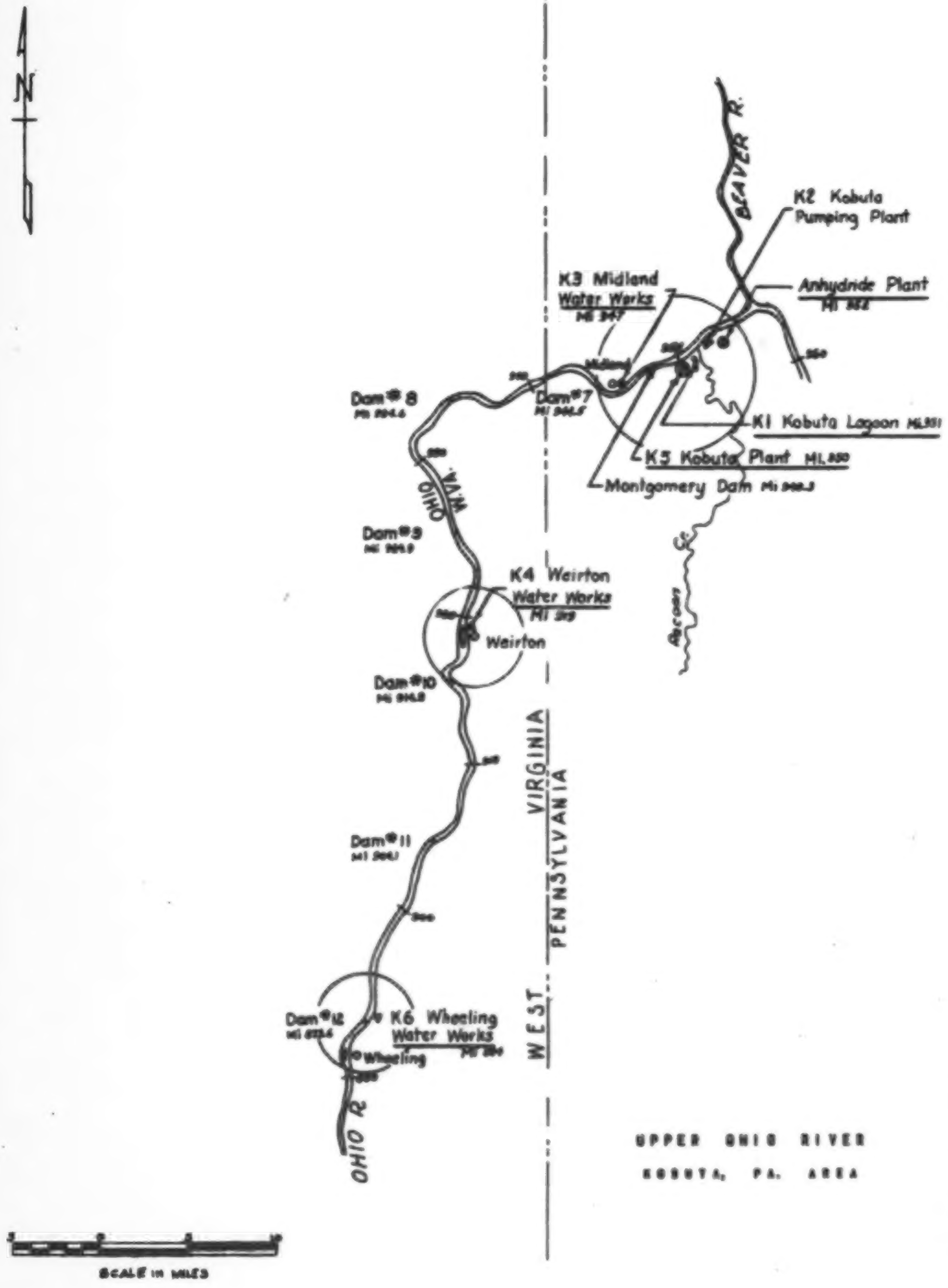
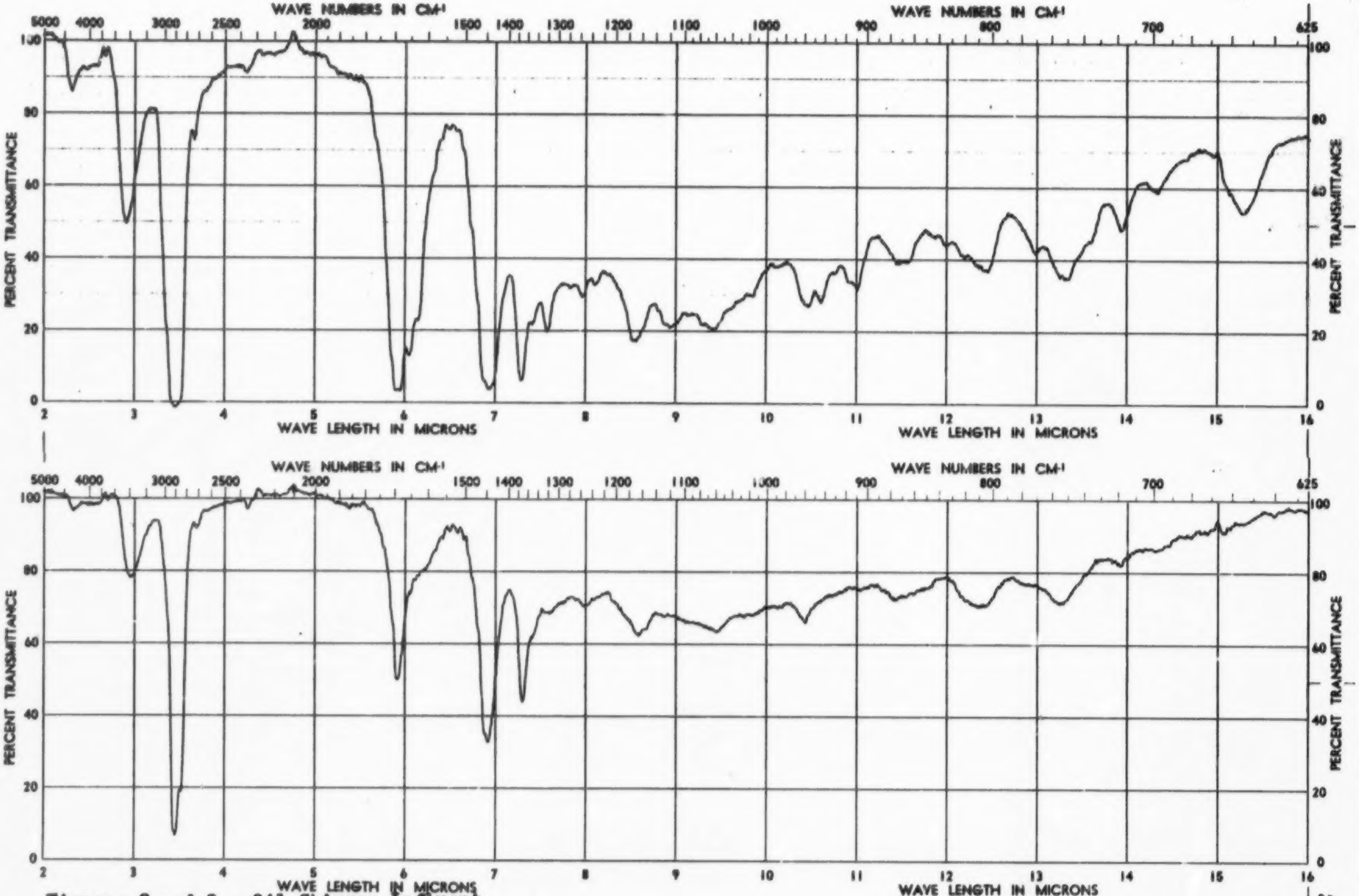
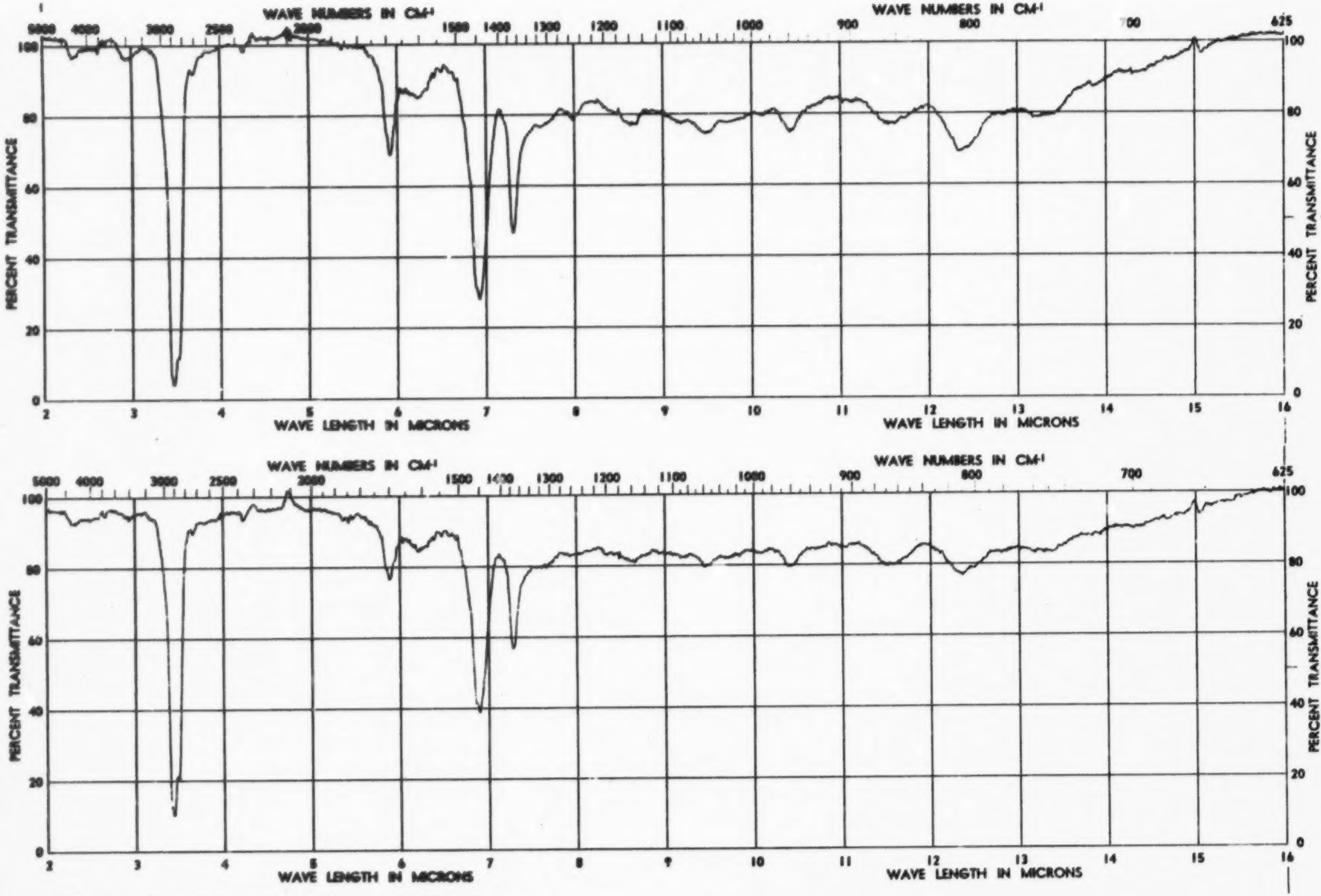

N
BEAVER R.
K2 Kobuta Pumping Plant
Anhydride Plant
K3 Midland Water Works
Midland
Dam #8
Dam #7
K1 Kobuta Lagoon
K5 Kobuta Plant
Montgomery Dam
OHIO
W.VA.
Dam #9
K4 Weirton Water Works
Weirton
Dam #10
WEST VIRGINIA
PENNSYLVANIA
Dam #11
Dam #12
K6 Wheeling Water Works
Wheeling
OHIO R.
UPPER OHIO RIVER
KOBUTA, PA. AREA
SCALE IN MILES

FIGURE 1

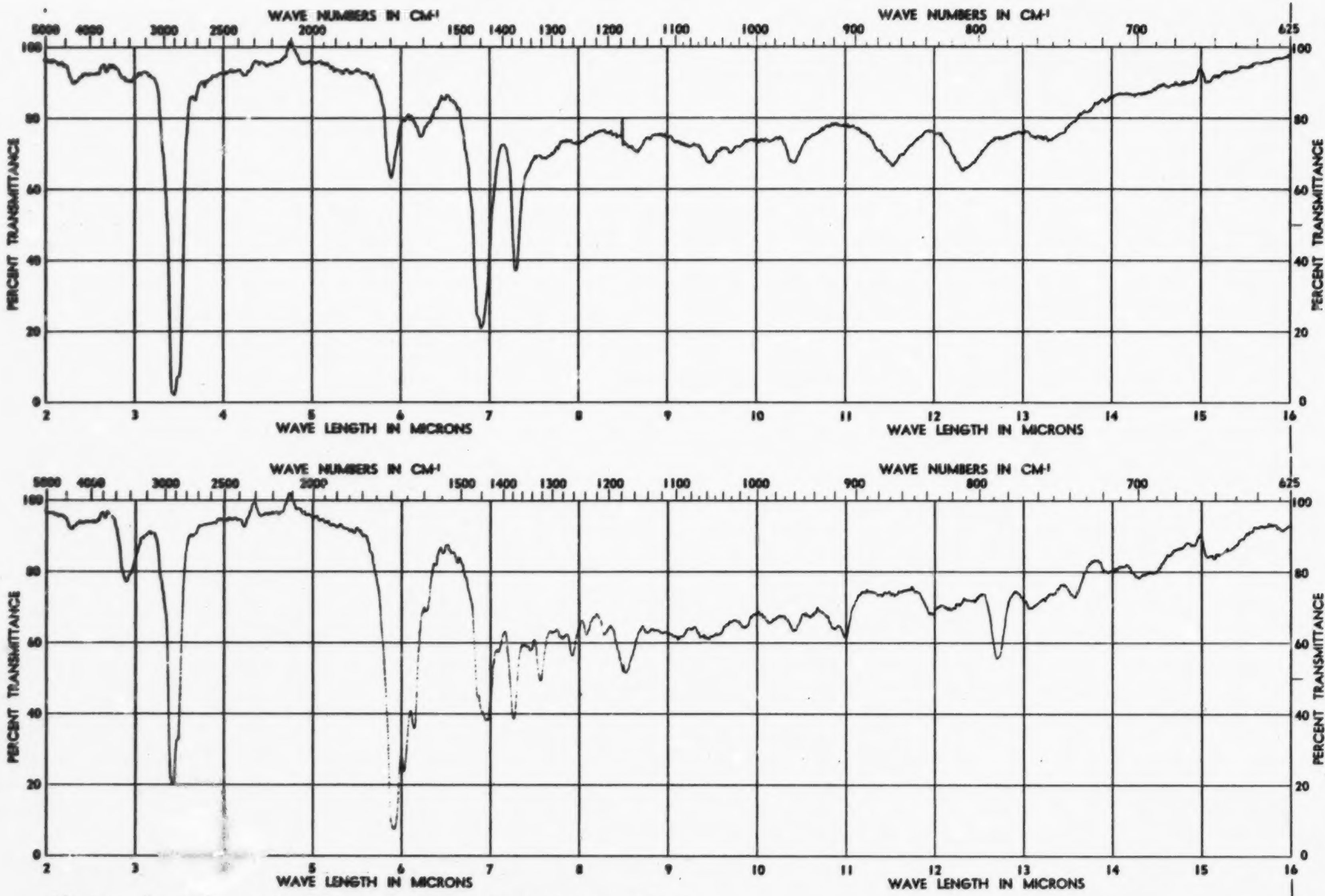


Figures 2 and 3 - Oil Skimmer Influent
Neutral Fractions 1 and 2

21-a



Figures 4 and 5 - Oil Skimmer Influent
Neutral Fractions 3 and 4



Figures 6 and 7 - Oil Skimmer Influent Neutral Fraction 5
and Lagoon Effluent Neutral Fraction 1

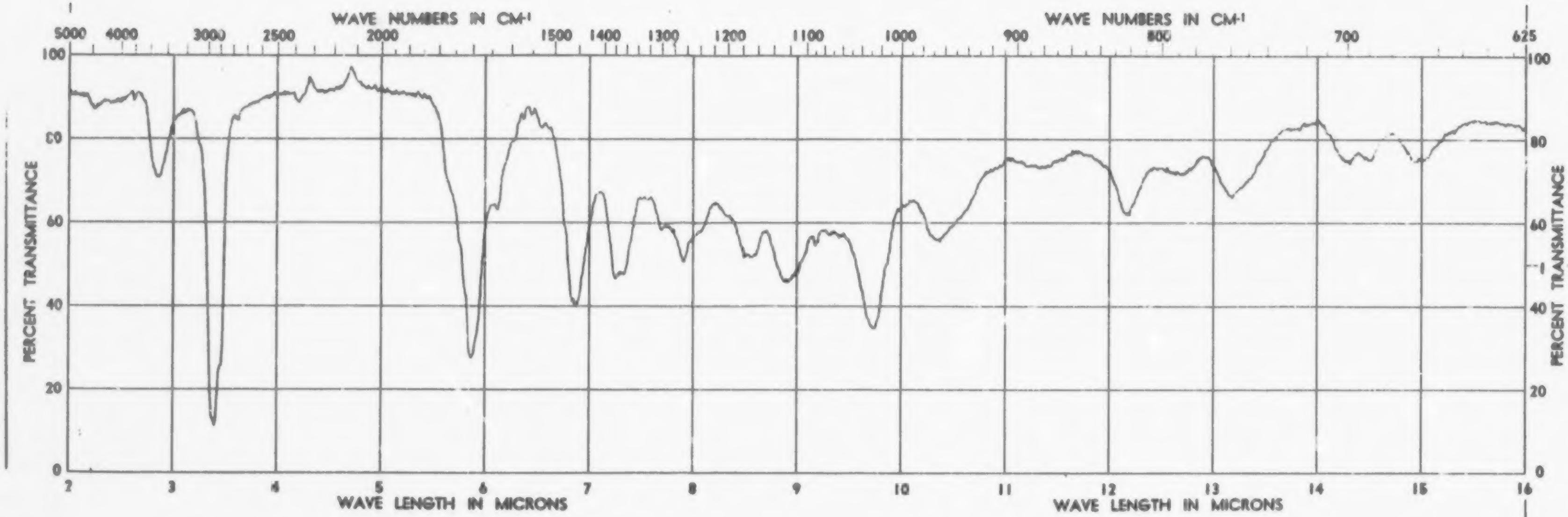


Figure 8 - Weirton, West Virginia
Neutral Fraction 1

REFERENCES

(1) Middleton, F. M., Braus, Harry, and Ruchhoft, C. C. "The Application of the Carbon Filter and Countercurrent Extraction to the Analysis of Organic Industrial Wastes." Proceedings of Seventh Industrial Waste Conference, Purdue University, May, 1952, p. 439.

(2) Craig, L. C., and Craig, D. "Technique of Organic Chemistry." A. Weissberger, Ed. Vol. 3, Ch. 4, Interscience Publishers, New York, 1950.

(3) Braus, Harry, Middleton, F. M., and Walton, Graham. "Organic Chemical Compounds in Raw and Filtered Surface Waters." Anal. Chem. 23, 1160, Aug. (1951).